ORGANIC OXIDATIONS BY MEANS OF POTASSIUM PERMANGANATE AND POTASSIUM PERSULFATE

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ORGANIC OXIDATIONS BY MEANS OF POTASSIUM PERMANGANATE AND POTASSIUM PERSULFATE

By

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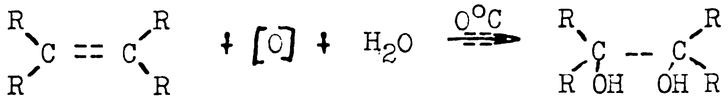
INTRODUCTION

A. POTASSIUM PERMANGANATE

For some time potassium permanganate and potassium dichromate have been used as strong oxidants for organic compounds. Generally these have been used in excess and in acidic solutions. These conditions result in rupture of an ethylenic type double bond with the resulting products being, in many cases, carbon dioxide and water, or something like acetic acid which isn't further oxidized. An example of this is the qualitative test for alkenes, which rapidly decolorize a dilute aqueous solution of potassium permanganate and sulfuric acid.

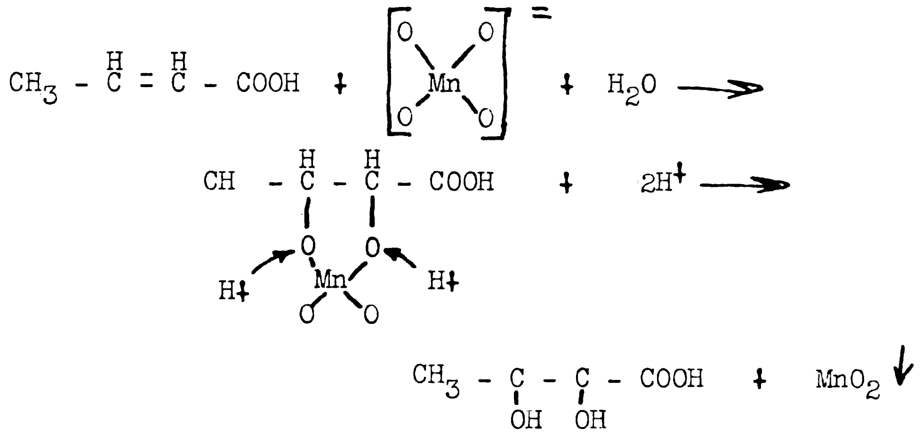
It has also been established that when alkaline potassium permanganate is used as oxidizing agent on alkenes, avoiding an excess of reagent, it is possible to isolate, as the primary reaction product, the corresponding saturated dihydroxy compound. Fieser (1) states that the process consists of the addition to the double bond of two hydroxyl groups, which may be considered to be derived from the combination of an oxygen atom, supplied by the potassium permanganate, with a molecule of water.



$$R_2C{=}CR_2 + [O] + H_2O \xrightarrow{0^{\circ}C} R_2C(OH){-}C(OH)R_2$$

Alkaline potassium permanganate is milder in action than the acidic solution and makes this reaction possible.

The investigator believes that at room temperature, in neutral to slightly alkaline media, the reaction consists of the formation of an intermediate complex, with a resulting disproportionation to the corresponding saturated dihydroxy compound. It also appears that this intermediate complex is formed with the manganate ion and not with the permanganate ion, as follows:



The setting down of this last equation brings us to the object of this study, at least as far as the potassium permanganate portion is concerned. It has been the purpose of the investigation to make a study of the neutral to slightly alkaline potassium permanganate mechanism for the oxidation of ethylenic type double bonds to form the corresponding saturated α,β dihydroxy compounds, especially with regard to crotonic acid, maleic acid, and allyl alcohol.

The suggested hypothesis is: the mechanism of neutral to slightly alkaline potassium permanganate oxidations of ethylenic type double bonds, to the corresponding saturated α,β dihydroxy compounds, proceeds predominantly by the step of manganate ion going to manganese dioxide, while the step of permanganate ion going to manganate ion contributes little, if any, to this formation of corresponding saturated α,β dihydroxy compounds directly.

This hypothesis was stated previous to the study and the following experimental work was so planned as to prove, or disprove, this statement as completely as possible.

B. POTASSIUM PERSULFATE

The persulfuric acids, permonosulfuric acid (Caro's acid) H_2SO_5, and perdisulfuric acid $H_2S_2O_8$, are derived from hydrogen peroxide. Caro's acid may be considered to be formed by replacing one H of HOOH

with HSO_3^- to yield HSO_3-OOH, and the persulfuric acid, $H_2S_2O_8$, may be considered to be derived from the substitution of both H of HOOH, with two HSO_3^- to yield HSO_3OO-HSO_3.

Caro's acid has been shown to attack many organic substances explosively, such as benzene or phenol. "There is a characteristic difference between the oxidizing effect of the two acids; Caro's acid, which has the hydrogen peroxide radical unprotected, oxidizes hydrogen iodide instantly and converts aniline into nitrosobenzene and nitrobenzene, while perdisulfuric acid does not give these reactions, though ferrous salts are immediately oxidized by perdisulfuric acid." (2) These two acids, however, don't give the characteristic reactions of hydrogen peroxide. Hydrolysis of the perdisulfuric acid by means of sulfuric acid results in the following equation:

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$$

A stable, pure, potassium salt of the perdisulfuric acid is available but little is known of the salts of Caro's acid.

It was from this preceding material that the investigator first thought that oxidation of organic compounds, using potassium persulfate, would result in somewhat similar end products to those derived from potassium permanganate oxidations. The hydrolysis of this potassium salt was to be accomplished by using a strongly alkaline media, rather than acidic, and at room temperature, thinking that the reaction would be milder, as in the case of neutral to alkaline potassium permanganate oxidations, than that predicted in acid media with organic compounds. This alkaline hydrolysis would probably result in the following equation:

$$S_2O_8{}^= + H_2O \rightarrow HSO_5{}^- + SO_4{}^= + H^+$$

Regardless of the actual mechanism, whether it was the HSO_5^- or a free radical mechanism, as postulated by some people, the object of the

study herein contained remains a study of just what types of organic compounds may be oxidized by potassium persulfate solution, in strongly alkaline media, and an attempt to determine what the reaction end products might be.

The suggested hypothesis which was followed in this investigation was: potassium persulfate in strongly alkaline media may be used as a mild organic oxidant.

HISTORICAL

A. POTASSIUM PERMANGANATE

Stamm (3) recognized the fact that the oxidation of many compounds by the old form of permanganate titration, in which the material to be oxidized was in acid solution and permanganate was then titrated in, to the first appearance of a permanent pink, was too slow to give a good titration. Organic compounds are notoriously slow in being oxidized by permanganate. The principle of the new procedure developed by Stamm for titrations with alkaline permanganate solution is that the oxidation of the material being determined involves only the first, very rapid, partial reaction of the permanganate, that is, the conversion of permanganate to manganate, while the slow, second partial reaction, manganate to manganite is not allowed to occur.

The procedure used by Stamm, now called the Stamm reaction, is based on the addition of excess permanganate to an alkaline solution of the organic compound to be oxidized and a back titration of the excess permanganate, after five to twenty minutes of reaction time, with standard formate in the alkaline medium or acidification and oxalic acid back-titration.

Stamm allowed the permanganate to go to manganite (manganese dioxide) during the five to twenty minutes of reaction time and then added a barium salt before the back-titration of the excess permanganate with formate. This barium salt was added because in this back-titration Stamm wished to stop the reduction of the permanganate at the manganate stage, to speed up the titration. Barium salts were chosen for this purpose because of the insolubility of the precipitated barium manganate (S. P. = 2.46×10^{-10}). The manganate ion produced, by the reduction

of the permanganate with formate, is consequently bound by the barium ion so rapidly that it is effectively removed from any further action of the reducing agent and the removal is so complete that in the absence of permanganate ion, or other colored materials, the supernatant liquid is colorless.

Stamm was thus primarily interested in increasing the speed of permanganate titrations with reductants. His results of the organic oxidations were expressed as equivalents of oxygen consumed and the oxidation products formed.

The present investigation, differs from Stamm's in that the barium salt is added to the neutral to slightly alkaline solution of the organic compound before the permanganate is added and no excess of potassium permanganate is used. This large excess of barium ion precipitates the manganate ion as soon as it forms in the breakdown of the permanganate, and if it is the manganate ion which is the active agent in the oxidation to the corresponding saturated dihydroxy compound, there should be little, if any, dihdroxy compound formed. Identical reactions were run, with the exception of the addition of barium ion, and a comparison of results made.

B. POTASSIUM PERSULFATE

Kailan and Olbrich (4) studied the velocity of the decomposition of potassium persulfate at 25°C, both alone and in the presence of sulfuric acid. The results indicated a unimolecular reaction and agreed quantitatively with previous work. The speed of the reaction was found to be sensitive to ionic influences; in particular, H^+ and NO_3^- ions accelerated the reaction while $SO_4^=$ and K^+ ions retarded it. With a decrease in the partial pressure of oxygen over the solution, the velocity of the reaction did not increase and so the effect of substances like toluene, which accelerate the reaction, is not due to oxidation.

Kailan and Leisek (5) studied the velocity of the decomposition of persulfates in aqueous solution. The velocity of the decomposition of sodium persulfate alone and with the addition of sodium acid sulfate, sodium sulfate, sodium nitrate, sodium hydroxide, phosphoric acid, sodium acid phosphate, and sodium phosphate, was investigated as well as the decomposition velocity of potassium persulfate with the addition of potassium nitrate and hydroxide. The experiments were done at 99.4°C. With increasing concentration of the persulfates, the monomolecular velocity coefficient decreases. The sodium persulfate decomposes more rapidly than the potassium salt. The ions H^+, NO_3^-, and OH^-, and HPO_4^- accelerated the reaction while K^+, Na^+, and SO_4^{-2} ions had a retarding effect, with K^+ more than Na^+.

Rao, Ramanjaneyulu, and Rao (6) studied the reaction of potassium persulfate and potassium iodide. Sunlight, or even artificial light can accelerate a reaction that becomes suitable for quantitative analysis. A suspension of cuprous iodide in water was found to be an excellent catalyst for the reaction of potassium persulfate and potassium iodide, and could be used for determining potassium persulfate. For best results it is necessary to have the iodide at a concentration of twenty to fifty times that of the potassium persulfate. The ions Ag^+, Hg^{+2}, Ce^{+3}, Co^{+2}, Ni^{+2} and Mn^{+2} did not catalyze the reaction between persulfate and iodide, either in neutral or acid solution but Fe^{+2} and Fe^{+3} salts were good catalysts.

No literature has been found on using potassium persulfate as an oxidizing agent for organic compounds in strongly alkaline media and the following study was so planned as to bring out some usable material on this subject.

EXPERIMENTAL

A. POTASSIUM PERMANGANATE

1. Preparation of reagents

(a.) Sodium manganate

A nickel crucible was used for the fusion of sodium hydroxide and potassium permanganate. The reaction taking place was:

$$4\mathrm{Na}\curvearrowright\mathrm{OH} + 2\mathrm{K}\curvearrowright\mathrm{Mn}\curvearrowright\mathrm{O}_4 == 2\mathrm{Na}_2\curvearrowright\mathrm{MnO}_4 + \mathrm{K}_2\mathrm{O} + [\mathrm{O}]$$

From this equation it can be seen that it is necessary to use two moles of sodium hydroxide to every mole of potassium permanganate. The investigator, to insure reduction of all the permanganate, used a ratio of three to one. As much as the volume of the crucible was comparatively small, one-half mole (20g) of sodium hydroxide and one-sixth mole (26g) of permanganate were used.

The hydroxide pellets were first placed in the crucible and melted carefully to a fluid state, then permanganate was added from the tip of a spatula, a few grains at a time. When approximately one-half of the permanganate had been added, the amount of spattering decreased and allowed larger quantities of permanganate to be added safely. The bottom of the crucible was kept at a red heat throughout the fusion.

To remove the sodium manganate from the crucible it was found best to let the mass cool down slightly, from the red heat, and then to use a nickel spatula in loosening the mass and dumping it on a watch glass. The sodium manganate and potassium oxide thus formed was placed in a large, stoppered test tube.

It was found that if the container was tightly stoppered the sodium manganate could be kept up to three months without appreciable oxidation back to permanganate. This stability was no doubt due to the excess sodium hydroxide, because under very strongly alkaline conditions and

in the absence of air, sodium manganate is quite stable.

The investigator also used barium manganate which was prepared by dissolving as much of the fusion material as possible in distilled water and then adding an excess of a saturated barium chloride solution. The precipitated barium manganate was filtered off and dried on a filter paper.

(b.) <u>0.1 M Crotonic acid</u>

A five hundred ml solution was made up by weighing out analytically, 4.3045g of crotonic acid, dissolving in water and diluting to five hundred ml. The solution was stored in a glass stoppered volumetric flask.

(c.) <u>0.1 M Maleic acid</u>

A five hundred ml solution was made up by weighing out analytically 5.8035g of maleic acid, dissolving in water and diluting to five hundred ml. The solution was stored in a glass stoppered volumetric flask.

(d.) <u>0.0328 M Allyl alcohol</u>

A one hundred ml solution was prepared by weighing out 0.1906g of pure allyl alcohol in a sealed tube and then breaking the tube under water and diluting to one hundred ml in a glass stoppered one hundred ml volumetric flask. The molarity was calculated from the weight of allyl alcohol taken.

2. <u>Methods of calculation</u>

(a.) <u>Sodium periodate method of analysis</u>

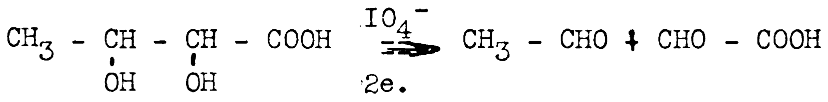
$$\left[(\text{ml x normality } IO_4^-) - \left[(\text{ml x N arsenite}) - (\text{ml x N } I2)\right]\right] \begin{array}{l}\text{x factor to convert}\\ \text{aliquot over to}\\ \text{total dilution}\end{array} = \begin{array}{l}\text{milli-equivalents}\\ \text{of } IO_4^- \text{ used}\end{array}$$

$$\begin{array}{c}\text{grams of } KMnO_4\\ \text{reductant converted}\\ \text{to dihydroxy form}\end{array} = \frac{\text{mole wt. reductant}}{\begin{array}{c}\text{Equivalents x 1000}\\ \text{per mole } IO_4^-\end{array}} \text{ x } \begin{array}{l}\text{m.e.} IO_4^-\\ \text{used}\end{array}$$

$$\% \text{ Conversion} = \frac{\text{g. } KMnO_4 \text{ reductant converted}}{\text{g. } KMnO_4 \text{ reductant started with}} \times 100$$

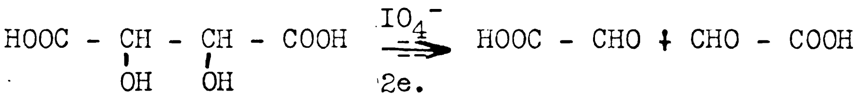
To obtain the equivalents per mole of periodate, the particular α,β dihydroxy compound analyzed for must be taken into account.

α,β dihydroxy crotonic acid



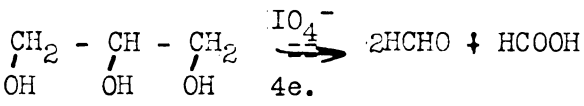
$$CH_3 - \underset{OH}{CH} - \underset{OH}{CH} - COOH \xrightarrow[2e.]{IO_4^-} CH_3 - CHO + CHO - COOH$$

α,β dihydroxy maleic acid



$$HOOC - \underset{OH}{CH} - \underset{OH}{CH} - COOH \xrightarrow[2e.]{IO_4^-} HOOC - CHO + CHO - COOH$$

Glycerol



$$\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2} \xrightarrow[4e.]{IO_4^-} 2HCHO + HCOOH$$

To find the number of equivalents per mole of periodate, the formula 2n-2 can be applied.

n = the number of carbon atoms, adjacent to each other, which have hydroxyl groups attached to them and when not part of a carboxyl group.

As α,β dihydroxy crotonic acid has two such carbon atoms, $(2 \times 2) - 2 = 2$ equivalents per mole of periodate, etc..

(b.) Perchlorato-cerate method of analysis

$$\left[(\text{ml.} \times NCe^{+4}) - (\text{ml} \times NCe^{+4} \text{ reductant})\right] \times \text{factor to convert aliquot over to the total dilution}$$

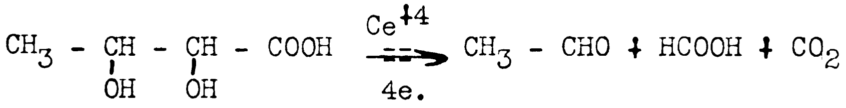
$$= \text{milli-equivalents of } Ce^{+4} \text{ used}$$

$$\text{grams of } KMnO_4 \text{ reductant converted to } \alpha,\beta \text{ dihydroxy form} = \frac{\text{Mole wt. reductant}}{\text{Equivalents per Mole } Ce^{+4} \times 1000} \times \text{m.e. } Ce^{+4} \text{ used}$$

$$\% \text{ Conversion} = \frac{\text{g. of } KMnO_4 \text{ reductant converted}}{\text{g. of } KMnO_4 \text{ reductant started with}} \times 100$$

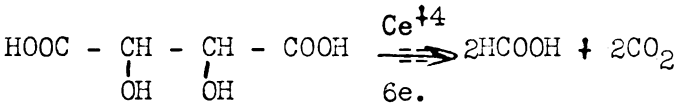
Again, to obtain the equivalents per mole of Ce^{+4}, the particular α,β dihydroxy compound analyzed for must be taken into account.

α,β dihydroxy crotonic acid



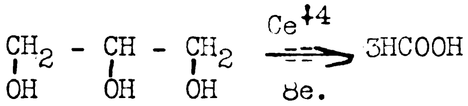
$$\mathrm{CH_3 - \underset{OH}{CH} - \underset{OH}{CH} - COOH \xrightarrow[4e.]{Ce^{+4}} CH_3 - CHO + HCOOH + CO_2}$$

α,β dihydroxy maleic acid



$$\mathrm{HOOC - \underset{OH}{CH} - \underset{OH}{CH} - COOH \xrightarrow[6e.]{Ce^{+4}} 2HCOOH + 2CO_2}$$

Glycerol



$$\mathrm{\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2} \xrightarrow[8e.]{Ce^{+4}} 3HCOOH}$$

To find the number of equivalents per mole of Ce^{+4}, the formula $2n + 2$ can be applied.

n = the number of carbon atoms adjacent to each other, which have hydroxyl groups attached to them and when not part of a carboxyl group.

As α,β dihydroxy crotonic acid has two such carbon atoms, $(2 \times 2) + 2 = 6$ equivalents per mole of Ce^{+4}, etc..

3. Procedures, calculated results, and discussions

(a.) Crotonic acid

The first oxidations were run by using the manganate ion as the oxidizing agent, and was used in the form of sodium manganate and barium manganate.

Run #1

In this run, using barium manganate, the fusion mixture was dissolved, as much as could be made to go into solution, in one hundred ml of water and then a saturated solution of barium chloride was added to precipitate the barium manganate. This was then filtered off and dried.

The reactants, 15g (0.06 moles) of barium manganate and 7.2g (0.08 moles) of crotonic acid, were in approximately equimolar proportions. Each reactant was dissolved, as much as could be, in one hundred ml of water before mixing, the crotonic acid not being neutralized first. After adding the barium manganate suspension to the solution of crotonic acid, the mixture was placed on a mechanical shaker for one-half hour, the time it took for the solution to turn brown with precipitated manganese dioxide.

This manganese dioxide and the undissolved barium manganate was filtered off and the filtrate was diluted to five hundred ml. Of this five hundred ml dilution a fifty ml aliquot was taken for analysis by periodate.

As a means of analyzing, twenty-five ml of 0.2 N sodium periodate was added to the aliquot from a burette and allowed to stand for four hours. At the end of this time twenty-five ml of saturated sodium bicarbonate and five ml of 20% potassium iodide solutions were added and the flask swirled until the full iodine color developed. Following this, twenty-five ml of 0.2 N arsenite solution was added from a burette to completely decolorize the solution, and the excess arsenite was back-titrated, using 0.1460N iodine solution, which was standardized against the arsenite.

#1 Took 9.0 ml of 0.1460 N I_2

Run #2

This run was made using 16g of sodium manganate and 9.1g of crotonic acid, which were then in the ratio of 0.1 mole to 0.1 mole. The same procedure was followed with the exceptions that the crotonic acid was

neutralized with sodium hydroxide before mixing with the sodium manganate suspension and the shaking time was increased to one and three-quarters hours.

#2 Took 23.2 ml of 0.1460N I_2

Run #3

This run was made using 7g of sodium manganate and 4g of crotonic acid, making a ratio of 0.05 moles to 0.05 moles. This contained just half the quantity of reactants as the previous run and the crotonic acid was neutralized to methyl orange with sodium hydroxide, which is a little more on the acid side than the previous run. The shaking time was cut to one-quarter hour, the time it took for the green manganate coloration to completely change to the brown color of precipitated manganese dioxide. To eliminate the tedious work of filtering off the manganese dioxide the investigator added 5.7g (0.05 moles) of sodium bisulfite and warmed before acidifying with 1:5 sulfuric acid, which soon destroyed the brown precipitate of manganese dioxide. To eliminate the excess bisulfite, the solution was brought to boiling and held there for fifteen minutes, until there was no odor of sulfur dioxide given off. The solution was cooled and diluted to five hundred ml.

For analysis a fifty ml aliquot was taken and the procedure of previous runs repeated.

#3 Took 34.0 ml of 0.1432N I_2

Run #4

The exact same procedure was used, as that in #3, with the same quantities of reactants and removal of manganese dioxide with sodium bisulfite.

#4 Took 33.55 ml of 0.1432N I_2

Run #5

This run was an attempted oxidation using potassium permanganate, but in a solution containing, in addition to the neutralized crotonic acid, an excess of barium ion which consists essentially of trying to oxidize by means of the step, permanganate ion going to manganate ion.

The reactants consisted of 26g (1/6 mole) of potassium permanganate, 13g (1/6 mole) of crotonic acid and twenty-five ml of a saturated barium hydroxide solution. The crotonic acid was completely dissolved in one hundred and fifty ml of water and then the barium hydroxide was added to this solution. When this solution was thoroughly mixed, the potassium permanganate, which itself was dissolved in one hundred ml of water, was poured in. This mixture was then placed on the mechanical shaker for one-half hour till the brown manganese dioxide color appeared and none of the permanganate color was left. The precipitated manganese dioxide was filtered off, instead of adding sodium bisulfite, and the clear solution was diluted to five hundred ml.

For analysis a fifty ml aliquot was taken, twenty-five ml of 0.2N periodate was added and the solution allowed to stand for one hour. At the end of this time twenty-five ml of saturated sodium bicarbonate and five ml of twenty percent potassium iodide was added. When the iodine was completely liberated, twenty-five ml of 0.2N arsenite was added and the excess arsenite was back-titrated with 0.1420N iodine to a starch end point.

#5 Took 0.1 ml of 0.1420N I_2

CROTONIC ACID OXIDATIONS

Oxidant	Run	m.e. IO_4^-/500 used	g Crotonic/500 Converted	g Crotonic/500 Started	% Conversion
$BaMnO_4$	# 1	13.14	0.564	7.20	7.84
Na_2MnO_4	2	33.80	1.632	9.15	17.85
Na_2MnO_4	3	48.70	2.095	8.10	25.90
Na_2MnO_4	4	48.00	2.070	4.00	51.70
$KMnO_4 + Ba^{++}$	5	0.14	0.006	13.50	0.04

Discussion

By looking at the tabulated percent conversions above it can be seen that the results, formation of corresponding saturated dihydroxy compounds, when the oxidation step of manganate ion going to manganese dioxide was utilized, are at least twenty times greater than when the oxidation was stopped at the formation of the manganate ion, that is, when the step of permanganate ion going to manganate ion was utilized.

The explanation of what occurs in the permanganate to manganate ion step is difficult. The permanganate ion is visibly reduced to the manganate ion, which is then trapped out of the reaction by barium ion, yet periodate analysis, which is specific for 1,2 glycols, indicates very little dihydroxy compound formed. The only explanation that is reasonable is that in this step some of the reductant is oxidized but not to the corresponding saturated dihydroxy compound. In other words, this initial reaction in these permanganate oxidations of ethylenic type double bonds is just so much wasted energy, as far as the formation of corresponding dihydroxy compounds are concerned, using up reductant but producing very little desired product. If this theory is true, a better conversion should be obtained when starting directly with the manganate ion than when starting with permanganate because in the direct approach no reductant is used up in wasted energy, thus cutting down the amount available for conversion when the manganate ion has been attained. The limited results, indicated in the tabulated chart above, supports this better conversion theory but is insufficient data to base much on.

All that the data supports is that the percentage of conversion of crotonic acid to the corresponding saturated dihydroxy compound is far greater when the manganate ion is used at the oxidant than when permanganate ion is used only to the manganate ion.

Unfortunately, even though the work was only exploratory, in preparation for a more comprehensive study, the investigator varied the weight of each crotonic acid sample run. However, the equi-molar ratios of the oxidant and the crotonic acid were maintained and some comparison is justified on this basis.

The low percent conversion obtained in the attempted oxidation using barium manganate as oxidant was not due, primarily, to the ineffectiveness of the manganate ion, but rather, to the low solubility of barium manganate in water. This factor strongly limited the supply of manganate ion free in the solution, so that it just wasn't available for use as an oxidant.

The percent conversions in each of the three cases where sodium manganate was used as the oxidant do not compare too closely, but, as was stated above, the weights of the original crotonic acid samples varied. At least it may be seen that the conversions, when using sodium manganate as the oxidant, were much higher than when the oxidation was initiated with potassium permanganate and stopped at the manganate ion by addition of barium ion.

Run #6

At this point it appeared that there was sufficient evidence supporting the hypothesis to warrant shifting over to a totally liquid

reaction system, with the exception of possibly adding solid barium salts to supplement that used in a saturated solution, in the cases where it was to be used at all that is.

This run consisted of taking twenty-five ml of 0.1 M crotonic acid, four samples in all and placing them in three hundred ml Erlenmeyer flasks. All four samples were neutralized with sodium hydroxide and then each received twenty-five ml of 0.1116 M potassium permanganate, with no barium ion added. This amount of permanganate was used because if in excess, it would attack the dihydroxy compound formed and break it down.

The samples were shaken on a mechanical shaker for one hour and then the precipitated manganese dioxide was filtered off and the four clear solutions were diluted to five hundred ml.

For analysis twenty ml aliquots were removed from each of the four dilutions and run individually as outlined below. To the twenty ml aliquots, ten to twenty ml of 12 M perchloric acid was added from a graduate and then twenty-five ml of 0.1024N perchlorato-cerate solution was added from a burette. The reactions were allowed to proceed for one hour, before titrating the excess perchlorato-cerate present. For this determination, two methods were employed; one iodometric and the other using 0.1106N ferrous sulfate for back-titration.

In the iodometric method, one-half gram of potassium iodide was added to each of the four aliquot samples, which were oxidized with perchlorato-cerate solution, and the iodine that was liberated was titrated with 0.1042N sodium thiosulfate to a starch end point.

#1	Took 20.45 ml of 0.1042N thiosulfate	
#2	20.65 ml	
#3	20.55 ml	
#4	20.60 ml	

In the ferrous sulfate method of excess perchlorato-cerate titration, ferroin was used as internal indicator. The four aliquots concerned, were run identically with those in the immediately preceding determination, up to the back-titration of the excess perchlorato-cerate.

#1 Took 19.4 ml of 0.1106N ferrous sulfate

#2 19.5 ml

#3 19.5 ml

#4 18.6 ml

To provide a conclusive check, analyses were run on four more aliquots by using the periodate procedure. The same five hundred ml dilutions, as used above, were used and twenty ml aliquots from these were taken. To each of the six, twenty ml aliquots, doubles on numbers two and three, was added two drops of phenolphthalein indicator. The hydrogen ion concentration was then adjusted with 1 M hydrochloric acid to a just colorless end point. The six aliquots were then each reacted with ten ml of 0.2N periodate for two hours. The next step was to add, from a burette, 0.1N sodium hydroxide to each of the six flasks until a light pink color persisted. This step, and the ones following, were completed on each aliquot before going on to the next. Twenty-five ml of saturated sodium bicarbonate and ten ml of twenty percent potassium iodide were added and the flask swirled just long enough for all the iodine to be liberated, two to five minutes. Ten ml of 0.2N arsenite was then added to completely decolorize the solution, followed by a back-titration of the excess arsenite with 0.1124N iodine to a starch end point.

#1 Took 2.6 ml of 0.1124N I_2

#2 2.3 ml

#2 2.5 ml

#3 2.5 ml

#3 Took 2.6 ml of 0.1124N I_2

#4 3.0 ml

OXIDATION OF CROTONIC ACID WITH PERMANGANATE-NO BARIUM ION

Titrating	Aliquot	m.e. Ce^{+4}/500 used	g Crotonic/500 Converted	g Crotonic/500 Start	% Conversion
	# 1	9.50	0.2040	0.2152	95.0
Iodometric	2	10.25	0.2205		102.6
	3	10.50	0.2260		105.0
	4	10.25	0.2205		102.6
	# 1	10.50	0.2260	0.2152	105.0
$FeSO_4$	2	10.25	0.2205		102.6
	3	10.25	0.2205		102.6
	4	12.50	0.2690		125.0
		m.e. IO_4^-/500 used			
	# 1	7.30	0.3140	0.2152	146.0
	2	6.48	0.2785		129.5
I_2	2	7.02	0.3020		140.5
	3	7.02	0.3020		140.5
	3	7.30	0.3140		146.0
	4	8.42	0.3620		168.5
					Av. = 145.1

Discussion

The data obtained only supports the part of the hypothesis which concerns the manganate ion oxidation because the run was made using no barium ion to stop the oxidation at the manganate ion.

In so far as the manganate ion is difficult to use directly this indirect method of showing its effect was used. The permanganate ion to manganate ion step was represented by using potassium permanganate on the reductant which had had an excess of barium ion added, because this prevents the permanganate ion from being reduced any further than to the manganate ion. The manganate ion to manganese dioxide step was represented by using potassium permanganate on the reductant and allowing it to pass through the manganate ion all the way to manganese dioxide. This also contains the effects of the first step, but this is so small as not to be very important. The differential of the conversions of the two steps was what the investigator was looking for.

The means of back-titration of excess perchlorato-cerate in the analysis seems to make very little difference in the conversions obtained and so, in as much as the iodometric procedure is the most convenient, due to its stability and easily seen end point, the investigator preferred to use it in perchlorato-cerate back-titrations.

In comparing the analysis made by perchlorato-cerate oxidation with those made by periodate oxidation it is immediately noticed that the periodate procedure gives approximately forty percent higher conversions to the α,β dihydroxy compound. This is partially explained by the fact that perchlorato-cerate is much slower acting on this type of compound than is periodate, especially with the CH_3^- group adjacent to the bond which was to be broken. More will be said about these figures after the barium ion run, Run #8.

Run #7

To show the consequences of not following the standard procedure for periodate oxidation of α,β dihydroxy compounds, which was used in Run #6, namely the pH at the time the periodate is added and when potassium iodide is added, the investigator ran the following on the exact same five hundred ml dilutions of Run #6.

The aliquots were taken in the same manner but the pH wasn't adjusted to just acid before the periodate was added. Instead, aliquots #1, 2 and 3 were acid to litmus and #4 was basic to litmus. The twenty ml aliquots were allowed to react with twenty-five ml of 0.2N periodate for two hours. At this point ten ml of twenty percent potassium iodide was added and allowed to stand for one-quarter hour on #1 and one-half hour on #2, 3 and 4, before twenty-five ml of 0.1 M sodium bicarbonate was added. To decolorize the liberated iodine, 0.2N arsenite was run in; #1, 25 ml; #2, 27.0 ml; #3, 25 ml; #4, 25 ml.

The titration of the excess arsenite was made in the usual manner, titration of liberated iodine with sodium thiosulfate to a starch end point.

#1	Took 19.4 ml of 0.1124N I_2
#2	24.75 ml
#3	24.90 ml
#4	25.90 ml

IMPROPER PERIODATE ANALYSIS OF DIHYDROXY CROTONIC ACID

Aliquot	**m.e. Crotonic/500 Converted**	**g Crotonic Converted**	**g Crotonic Started**	**% Conversion**
#1	54.5	1.17	0.2152	Impossible

Discussion

This short example of the effect of pH on the results obtained in periodate analyses brings out the necessity of following a set system of analysis. The pH of the solution must be just barely acid to phenolphthalein at the time of addition of the periodate and, previous to the determination of the excess periodate, the pH must be brought back to just alkaline to phenolpthalein and an excess of $NaHCO_3$ added. The specificity of periodate for α,β dihydroxy compounds depends on the fact that it be used in neutral to slightly acid media.

In a neutral solution arsenite can be oxidized quantitatively by means of free iodine.

$$H_2AsO_3^- + I_2 + 2HCO_3^- \rightarrow H_2AsO_4^- + 2I^- + H_2O + 2CO_2$$

but in strongly acid solution arsenic acid can be reduced quantitatively to the trivalent condition by means of iodide ion, the above equation is reversed.

$$H_2AsO_4^- + 2I^- + 6H^+ \rightarrow As^{+3} + I_2 + 4H_2O$$

To accomplish a complete oxidation of the arsenic by iodine, the solution must be kept approximately neutral to phenolphthalein. This is usually accomplished by providing an excess of sodium bicarbonate. Strong alkali cannot be used because it reacts with iodine to form hypoiodite and iodide. A little sodium carbonate does no harm if added to an acid solution because the liberated carbon dioxide neutralizes the hydroxyl ion formed by hydrolysis of the carbonate.

The reason for making the solution just alkaline to phenolphthalein, previous to the addition of potassium iodide, to determine the excess periodate by means of arsenite followed by standard iodine solution, may be seen in the following equations:

$$\text{excess } IO_4^- + I^- + \underline{2H^+} \rightarrow IO_3^- + H_2O + \tfrac{1}{2}I_2$$

$$I_2 + AsO_3^{\equiv} + H_2O \rightleftharpoons AsO_4^{\equiv} + 2HI + \text{excess } AsO_3^{\equiv}$$

$$\text{excess } AsO_3^{\equiv} + \text{Std. } I_2 + H_2O \xrightarrow{\text{starch}} AsO_4^{\equiv} + 2HI$$

Run #8

For the oxidations using potassium permanganate with added excess barium ion, the investigator used one liter Erlenmeyer flasks to allow for the water needed to dissolve the barium salt. Twenty-five ml of 0.1 M crotonic acid was pipetted into each of four flasks and neutralized with sodium hydroxide. To each of these four flasks, twenty grams of solid barium hydroxide was added and then diluted with two hundred ml of water to dissolve the barium hydroxide. When the mixtures were thoroughly mixed, twenty-five ml of 0.1116M permanganate was pipetted into each, with the solutions turning blue, with the precipitated barium manganate, immediately. Each flask was then stoppered and placed on a mechanical shaker for one hour. The precipitated barium manganate and excess, undissolved barium hydroxide was then filtered off and the filtrates diluted to five hundred ml.

In the analysis twenty ml aliquots were pipetted from each of the four dilutions and subjected to periodate (twenty-five ml of 0.2N) oxidation, without adjusting the pH one way or another. Immediately upon adding the periodate a thick, gelatinous, white mass was formed. This was possibly caused by the precipitation of barium periodate because there was definitely an excess of barium ion in solution. Reasonable and consistant titrations were impossible.

As can be seen, it was necessary to remove the excess barium ion from the aliquots before proceeding with the analyses. Inasmuch as a saturated solution of sodium bicarbonate was to be added later, the investigator chose to use a saturated solution of sodium carbonate to precipitate the barium ion as barium carbonate, which was quite insoluble and could be easily filtered off. This sodium carbonate did not interfere with the following arsenite addition and analysis because in this step carbon dioxide was released and this neutralized the hydroxyl ion which was formed by hydrolysis of the carbonate in weakly acid media.

Four twenty ml aliquots were taken from the four dilutions, prepared as above, and ten ml of saturated sodium carbonate added to each aliquot. The barium carbonate precipitate was filtered off, two drops of phenolphthalein indicator added to each of the four aliquots, and the pH adjusted to just colorless with hydrochloric acid. The ten ml of 0.2N periodate was then added to each aliquot from a burette and the reaction was allowed to proceed for two hours. From this point on, each aliquot was handled completely before the next was begun. The pH was adjusted back to a light phenolphthalein pink with 0.1N sodium hydroxide, twenty-five ml of saturated sodium bicarbonate and ten ml of twenty percent potassium iodide added and the flasks swirled one or two minutes to completely bring out the iodine color. This color was then destroyed with ten ml of 0.2N arsenite and the excess arsenite back-titrated with 0.1124N iodine, to a starch end point.

#1 Took 0.6 ml of 0.1124N I_2
2 1.9 ml
3 1.0 ml
4 1.3 ml

As a final check, the investigator repeated the exact same method of analysis on aliquots from the same dilutions.

#1 Took 0.1 ml of 0.1124N I_2
2 1.3 ml
3 0.8 ml
4 6.3 ml

OXIDATION OF CROTONIC ACID WITH PERMANGANATE-BARIUM ION ADDED

Aliquot	m.e. IO_4^-/500 used	g Crotonic/500 Converted	g Crotonic/500 Start	% Conversion
# 1	1.69	0.0727	0.215	33.8
2	5.35	0.2300		107.0

OXIDATION OF CROTONIC ACID WITH PERMANGANATE-BARIUM ION ADDED (Con't.)

Aliquot	m.e. IO$_4^-$/500 used	g Crotonic/500 Converted	g Crotonic/500 Start	% Conversion
# 3	2.81	0.1210		56.3
4	3.65	0.1560		72.6
# 1	2.81	0.1210	0.215	56.3
2	3.65	0.1560		72.6
3	2.25	0.0966		45.0
4	17.25	0.7420		345.0
				Av. 64.4

Discussion

As was stated in the procedure, the excess barium ion had to be removed due to the precipitation of possibly barium periodate, which interfered with the determination of the percent conversion to the corresponding saturated α,β dihydroxy compound.

COMPARISON OF CROTONIC ACID CONVERSIONS

Titrating Agent	No Barium		Barium Added		Titrating Agent
	Aliquot	% Conversion	Aliquot	% Conversion	
Iodometric	#1	95.0	#1	33.8	I$_2$
	2	102.6	2	107.0	
	3	105.0	3	56.3	
	4	102.6	4	72.6	
FeSO$_4$	#1	105.0	#1	56.3	I$_2$
	2	102.6	2	72.6	
	3	102.6	3	45.0	
	4	125.0	4	345.0	

COMPARISON OF CROTONIC ACID CONVERSIONS (Con't.)

Titrating Agent	No Barium		Barium Added		Titrating Agent
	Aliquot	% Conversion	Aliquot	% Conversion	
	#1	146.0			
	2	129.5			
I_2	2	140.5			
	3	140.5			
	3	146.0			
	4	168.5			
		Av. = 145.1		Av. = 64.4	

The average percent conversion of the crotonic acid to the corresponding saturated α,β dihydroxy compounds, when barium ion was used to limit the oxidation step of potassium permanganate to that of permanganate ion going to manganate ion, was shown to be an average of 64.4 percent.

The average percent conversion in the cases where no barium ion was added, Run #6 where the same reactants and the same means of analysis were used, was shown to be 145.1 percent. The two averages, 64.4% and 145.1% are definitely unreasonable but may be compared because the exact same procedures were used on both, with the exception that the first, 64.4% was obtained using barium ion. The ratio of the two, percent conversions, favors the manganate ion step by a ratio of 2:1.

At this point there is sufficient evidence, in the case of crotonic acid, to state that the original hypothesis has been supported. The suggested hypothesis was: The mechanism of neutral to slightly alkaline potassium permanganate oxidations of ethylenic type double bonds, to the corresponding saturated α,β dihydroxy compounds, proceeds predominantly by the step of manganate ion going to manganese dioxide, while the step of permanganate ion going to manganate ion contributes little, if any, to this formation of corresponding saturated α,β dihydroxy compounds directly.

It is necessary to remember that the reactants in the oxidations, potassium permanganate and crotonic acid, were added in equi-molar quantities, which will not give one hundred percent conversion, but, will prevent the breaking of the dihydroxy bond, which happens when excess permanganate is present. The important point is that the results can be used to compare the effectiveness of the two different oxidation steps because equi-molar starting concentrations were used. In other words, the investigator was not concerned with the absolute results, but rather with the relative results obtained under identical conditions.

(b.) Maleic acid

The study of maleic acid was started in the same way as the crotonic acid study was, comparing the results obtained by using sodium manganate as the oxidant with those obtained by using straight permanganate and those obtained by using permanganate with excess barium ion added.

Run #1

To a three hundred ml Erlenmeyer flask 5.8g (0.05 moles) of maleic acid was added and this was completely dissolved in one hundred ml of water. In another flask, 7.1g (0.05 moles) of sodium manganate was dissolved, only partially, in one hundred ml of water, and this was then poured into the maleic acid solution, stoppered and placed on the shaker for one-quarter hour, till the green manganate color had completely changed to the brown of precipitated manganese dioxide.

The maleic acid wasn't previously neutralized due to the fact that the sodium manganate contained an excess of sodium hydroxide which took care of the acidity.

To eliminate the tedious task of filtering off the manganese dioxide, an acidified solution of sodium bisulfite was used, as in the crotonic acid procedures. The clear solution was then diluted to five hundred ml in preparation for analysis.

A fifty ml aliquot was taken from this five hundred ml dilution and twenty-five ml of 0.2N periodate solution was added. The stoppered flask was then placed on the shaker for one-half hour, taken off and twenty-five ml of saturated sodium bicarbonate and five ml of twenty percent potassium iodide was added. The liberated iodine was decolorized with twenty-five ml of 0.2N arsenite and the excess arsenite titrated with standard 0.1760N iodine.

#1 Took 24.7 ml of 0.1760N I_2

Run #2

The 5.8g (0.05 moles) of maleic acid was again dissolved in one hundred ml of water and, as there was no excess of sodium hydroxide present as in the sodium manganate run, was neutralized to litmus with sodium hydroxide. To this three hundred ml Erlenmeyer flask, with the maleic acid, twenty-five ml of a saturated barium chloride solution was added. In another flask 7.9g (0.05 moles) of potassium permanganate was dissolved in one hundred ml of water. When the maleic acid and barium ion were thoroughly mixed, the potassium permanganate solution was poured in, turning the solution first green and then to blue as the barium manganate formed. The reaction was allowed to proceed for one-quarter hour, till the potassium permanganate color was completely destroyed, and then the barium manganate was filtered off. A five hundred ml dilution was made up and a fifty ml aliquot taken for analysis by the periodate procedure, reacting with the periodate for one-half hour.

#2 Took 6.9 ml of 0.1760N I_2

Run #3

This run was made in the same manner as the immediately preceding one, up to the analysis, with the exception that 8.6g (0.05 moles) of barium hydroxide was used in place of barium chloride to supply the barium ion. This change had to be made because the analysis was to be made using a perchlorato-cerate solution in place of periodate, and this oxidant liberates chlorine from chloride solutions.

In the analysis, only a twenty-five ml aliquot of the five hundred ml dilution was pipetted out. To this was added ten ml of 12 M perchloric acid and twenty-five ml of 0.1N perchlorato-cerate, and then the flask was placed on the shaker for one-quarter hour. The back-titration of excess cerate was made with standard 0.1N sodium oxalate, using nitro-ferroin as indicator.

#3 Took 4.9 ml of 0.1N sodium oxalate

Run #4

This run was made in the same manner as run #3, with the exception that 15g of barium nitrate was used as the source of the barium ion. The oxidation was allowed one-half hour on the shaker before filtering off the barium manganate, diluting and continuing with the analysis. A twenty-five ml aliquot was analyzed by means of perchlorato-cerate.

#4 Took 11.0 ml of 0.1N sodium oxalate

Run #5

The same procedure was used as in runs 3 and 4 with the exception of the source of the barium ion, two hundred ml of saturated barium nitrate being used. For the analysis a fifty ml aliquot of the five hundred ml dilution was taken in place of a twenty-five ml aliquot. The concentration of perchlorato-cerate was kept at twenty-five ml of 0.1N solution and the reaction period was one-quarter hour.

#5 Took 10.65 ml of 0.1N sodium oxalate

Run #6

The potassium permanganate 7.9g (0.05 moles), was dissolved in one hundred and fifty ml of water and the maleic acid, 5.8g (0.05 moles), was also dissolved in the same volume of water and then neutralized to litmus with sodium hydroxide. The solution and suspension of potassium permanganate was left in its flask and the maleic acid solution was poured in. The flask was stoppered and placed on the shaker till the solution turned brown; one-half hour. The solution was filtered with difficulty and diluted to five hundred ml.

For analysis a twenty-five ml aliquot was taken, acidified with five ml of 72 percent perchloric acid and fifty ml of 0.1N perchlorato-cerate solution was added from a burette. The reaction was allowed to proceed for one-half hour and then the excess cerate was back-titrated with standard 0.1N sodium oxalate, using nitro-ferroin as internal indicator.

#6 Took 10.15 ml of 0.1N sodium oxalate

OXIDATION OF MALEIC ACID

Oxidizing agent used	**Run**	**m.e. IIO_4^-/500 used**	**g Maleic/500 Converted**	**g Maleic/500 Start**	**% Conversion**
Na_2MnO_4	#1	43.47	2.520	5.80	43.50
$KMnO_4+Ba^{++}$	2	12.15	0.705		12.15
		m.e. Ce^{+4}/500 used			
$KMnO_4+Ba^{++}$	3	40.20	0.779	5.80	13.40
	4	28.00	0.541		9.35
	5	14.40	0.278		4.80
$KMnO_4$	6	79.60	1.541	5.80	26.60

Discussion

The investigator realized that the procedure of roughly weighing out solid samples of the reactants and then attempting to dissolve them individually in limited amounts of water, before mixing, was a rough means of attacking the problem at hand but the ground work had to be laid before a more comprehensive approach was warranted.

The runs made brought out the fact that a saturated solution of barium hydroxide, plus some solid barium hydroxide, was the best source to ensure an excess of barium ion being present to precipitate the manganate ion as soon as it was formed.

As a whole the runs supported the investigator's original hypothesis, which was: the mechanism of neutral to slightly alkaline potassium permanganate oxidations of ethylenic type double bonds, to the corresponding saturated α,β dihydroxy compounds, proceeds predominantly by the step of manganate ion going to manganese dioxide, while the step of permanganate ion going to the manganate ion contributes little, if any, to this formation of corresponding saturated α,β dihydroxy compounds directly.

All the runs were made using the same amounts of reactants, 0.05 moles of each, so they can be compared roughly with each other.

Again, there is no definite proof as to what the oxidation step of permanganate ion to manganate ion produces but the analysis for α,β dihydroxy compound shows little of this material being formed in the step. When the manganate ion step is allowed to occur however, runs 1 and 6, the percent conversions are approximately three times greater than when stopped at the manganate ion.

Run #7

By means of a twenty-five ml pipette, three samples of standard 0.1 M maleic acid were transferred to two hundred ml Erlenmeyer flasks and each was neutralized with sodium hydroxide. The oxidant, twenty-five ml of 0.1116M potassium permanganate, was added to each maleic acid sample by means of a twenty-five ml pipette, resulting in a solution of approximately equimolar concentrations. The solutions turned brown immediately but they were shaken for two hours to ensure complete reaction. At the end of this time each sample solution was filtered to remove the precipitated manganese dioxide and give a clear solution, which was then diluted to five hundred ml. The analysis of these mixtures was carried out with 0.1020N perchlorato-cerate solution but the means of back-titration of the excess of this cerate was varied to include the use of an iodometric procedure, sodium oxalate and ferrous sulfate.

A twenty ml aliquot was pipetted out of each of the three dilutions into Erlenmeyer flasks. Ten to twenty ml of 72 percent perchloric acid was added to each, and from a burette, twenty ml of 0.1020N perchlorato-cerate solution was added to each. Due to the late hour in the day that the runs were started, the flasks were stoppered tightly and placed in a desk drawer over night. A slight red color developed in each flask on standing and upon investigation it was found to be due to a trace of manganous ion reacting with the cerate. The excess cerate was titrated with standard 0.2N sodium oxalate, using nitro-ferroin as internal indicator and taking to the first pale blue color. The red color due to the manganous ion interfered slightly because the end point had to be approached quite slowly, but once the end point was reached the solution turned a pale blue color correctly.

#1	Took 6.9 ml of 0.2N sodium oxalate
#2	6.9 ml
#3	6.85 ml

Six more twenty ml aliquots, two from each of the three five hundred ml dilutions, were each reacted with twenty ml of 0.1020N perchlorato-cerate, just as in the previous analyses using sodium oxalate, with the exception that the cerate was only allowed to react for one hour and the back-titration was made with 0.1126N ferrous sulfate, using ferroin as internal indicator.

#1 Took 14.95 ml of 0.1126N ferrous sulfate

1 14.75 ml

2 14.80 ml

2 ---

3 15.00 ml

3 14.95 ml

Three more twenty ml aliquots, each from a different dilution, were each reacted with twenty ml of 0.1020N perchlorato-cerate for one hour. The back-titration of the excess cerate was made by adding ten ml of twenty percent potassium iodide, swirling till the iodine was completely liberated and this was titrated with 0.1042N sodium thiosulfate to the first disappearance of the starch color.

#1 Took 15.65 ml of 0.1042N thiosulfate

2 15.00 ml

3 15.90

OXIDATION OF MALEIC ACID WITH PERMANGANATE-NO BARIUM ION

Titrating Agent	Aliquot	m.e. Ce^{+4}/500 used	g Maleic/500 Converted	g Maleic/500 Start	% Conversion
$Na_2C_2O_4$	# 1	16.50	0.3195	0.2902	110.0
	2	16.50	0.3195		110.0
	3	16.75	0.3240		111.6

OXIDATION OF MALEIC WITH PERMANGANATE-NO BARIUM ION (Con't)

Titrating Agent	Aliquot	m.e. Ce^{+4}/500 used	g Maleic/500 Converted	g Maleic/500 Start	% Conversion
$FeSO_4$	# 1	9.00	0.1740	0.2902	60.0
	1	9.50	0.1840		63.4
	2	9.25	0.1790		61.7
	3	8.75	0.1690		58.4
	3	9.00	0.1740		60.0
Iodometric	# 1	10.26	0.1985	0.2902	68.5
	2	12.00	0.2322		80.2
	3	9.50	0.1840		63.4

Discussion

As a means of determining whether the manganate ion takes part in the oxidation of double bonds, when using potassium permanganate, and still not have to start with the manganate ion itself, which is difficult to work with, a series of oxidations in neutral to slightly alkaline media were run, using potassium permanganate alone and allowing the reaction to proceed through the manganate ion step to manganese dioxide and also using potassium permanganate which had had excess barium ion added to it to stop the reaction at the manganate ion hence not allowing this ion to react.

The phase of the maleic acid study just described, where the potassium permanganate was allowed to proceed through the manganate ion step to manganese dioxide, brings out several points that should be considered. There is no doubt that the use of standard solutions of the reactants gives a better picture of the percent conversions because both reactants are in true solution and in sufficiently dilute concentrations to allow more complete reaction.

As to the best back-titrating agent to use, the investigator found the iodometric procedure faster but the sodium oxalate procedure had a slightly better reproducibility of titrations.

The percent conversions are compared, after the following study of barium ion effect, with the conversions obtained therein.

In venturing an opinion as to the difference found by computing the percent conversions by the three different means of back-titration, the investigator believes that the time of reaction was the predominating factor. In the sodium oxalate procedure, the perchlorato-cerate oxidation was allowed to continue over a period of approximately fifteen hours, while in the other two procedures only one hour was allowed. This information, added to the fact that perchlorato-cerate oxidations of α,β dihydroxy compounds are known to be slower than the corresponding periodate oxidations, would support the above time of reaction theory.

It would be interesting to make a further study of this perchlorato-cerate reaction, such as, rate or reaction, effect of increasing the perchlorato-cerate concentration, etc., but time does not allow this comprehensive a study.

The bisulfite method for the removal of manganese dioxide was not used because it was felt that the solutions were complex enough as it was.

Run #8

By means of a twenty-five ml pipette, four samples of standard 0.1 M maleic acid were transferred to two-hundred ml Erlenmeyer flasks and each was neutralized with sodium hydroxide. To each of these flasks ten grams of barium hydroxide was added and a dilution made with one hundred ml of water to get as much of the barium hydroxide into solution as possible. Each flask was thoroughly swirled and then twenty-five ml of 0.1116M potassium permanganate was pipetted into each flask, the flasks stoppered and placed on the shaker for two hours. The solutions went blue immediately, with the precipitation of barium manganate. This was filtered off and each sample was diluted to five hundred ml.

The analysis was made by perchlorato-cerate oxidation so that the percent conversions could be compared with those resulting from run #7, which had no barium ion added. Sodium oxalate back-titration of the excess cerate was first tried but the results couldn't be made to coincide at all. The investigator thought that the excess of barium ion still present in the solution was possibly responsible for this, giving an obscured end point with the nitro-ferroin indicator.

The iodometric procedure of back-titration was found to give fairly reproducible results and a good end point. Eight twenty ml aliquots, two from each of the four dilutions, were transferred to flasks by means of a twenty ml pipette. To each of these eight aliquots ten to twenty ml of seventy-two percent perchloric acid and twenty ml of 0.1020N perchlorato-cerate solution was added. These solutions were allowed to react for one hour in a closed desk drawer. At the end of this time ten ml of twenty percent potassium iodide was added and the flasks swirled until the liberation of iodine was complete, which was then titrated with 0.1042N sodium thiosulfate to a starch end point.

#1	Took 16.7 ml of 0.1042N thiosulfate
1	14.8 ml
2	15.7 ml
2	17.3 ml
3	19.5 ml
3	19.8 ml
4	18.8 ml
4	18.6 ml

OXIDATION OF MALEIC ACID WITH PERMANGANATE-BARIUM ION ADDED

Titrating agent	**Aliquot**	**m.e. Ce^{+4}/500 used**	**g Maleic/500 Converted**	**g Maleic/500 Start**	**% Conversion**
Iodometric	# 1	7.5	0.1450	0.2902	50.10
	1	12.5	0.2420		83.50
	2	10.0	0.1935		66.70
	2	6.0	0.1161		40.10
	3	0.5	0.0096		3.33
	3	0.0	0.0000		0.00
	4	2.0	0.0388		13.35
	4	2.5	0.0485		16.70

Discussion

The wide range obtained in the sodium thiosulfate titrations of the excess cerate, the iodine liberated from potassium iodide by the cerate that is, in the first two dilution analyses lead the investigator to believe that the reactions had not been completed and thus they were heavily discounted, in so far as consideration of their analyses was concerned. However, the rather close checks obtained between the dual titrations on each of the last two five hundred ml dilutions led the investigator to place some weight on their calculations. This discussion will be more or less limited to these last two dilutions.

Here again the barium ion could not be added in the form of barium chloride, due to the liberation of chlorine from chloride solutions by perchlorato-cerate. There is no absolute assurance that the manganate ion is precipitated immediately by the barium ion because only the color of the solution was used as an index in measuring this removal. To account for the appearance of at least a little oxidation, to the corresponding saturated dihydroxy compound, in the cases where barium ion was used, it might be theorized that some of the manganate ion was not trapped before it had attacked the double bonds. Before any more is said in this respect it would be wise to compare the data of the two different methods of oxidation of maleic acid; potassium permanganate with no barium ion added, in which case the manganate is allowed to enter into the oxidation; and potassium permanganate with barium ion added, in which case the permanganate can only go to the manganate ion in the oxidation.

COMPARISON OF MALEIC ACID CONVERSIONS

Titrating agent	No Barium		Barium		Titrating agent
	Aliquot	% Conversion	Aliquot	% Conversion	
	# 1	110.0	# 1	50.10	
$Na_2C_2O_4$	2	110.0	1	83.50	
	3	111.6	2	66.70	
			2	40.10	
	# 1	60.0	3	3.33	Iodometric
$FeSO_4$	1	63.4	3	0.00	
	2	61.7	4	13.35	
	3	58.4	4	16.70	
	# 1	68.5			
Iodometric	2	80.2			
	3	63.4			

Now that we have the picture before us, it can easily be seen that the manganate ion going to manganese dioxide oxidation step is quite necessary to oxidize the double bond of maleic acid to form the corresponding saturated dihydroxy compound. The percent conversions, in the cases where the manganate ion going to manganese dioxide step is allowed to react, by any of the means of determining the milli-equivalents of perchlorato-cerate used up in the analysis, far outstrip those of the series where the manganate ion is trapped and precipitated out of solution with barium ion before it has had an opportunity to react with the double bonds.

The investigator believes that these results would have been even more accentuated if the excess barium ion present in the dilutions had been removed prior to the analyses and if the faster acting periodate had been used in the analyses.

(c.) Allyl alcohol

Allyl alcohol was chosen as the source of double bonds in the third series of potassium permanganate oxidations, in neutral to slightly alkaline media with and without barium ion added. This compound was chosen, partly because of its ease of oxidation and partly to get away from the use of organic acids, such as crotonic and maleic acids.

Run #1

Four ten ml samples of 0.0328M allyl alcohol were transferred, by means of a ten ml pipette, to two hundred ml Erlenmeyer flasks. To approximate the milli-moles, 0.3280, of allyl alcohol, each flask received three ml of 0.1116M potassium permanganate, 0.3348 milli-moles, from a graduated pipette. The flasks were stoppered and placed on the shaker for four hours, to ensure complete reaction. The precipitated manganese dioxide was filtered off and each of the four clear solutions was diluted to two hundred and fifty ml.

For analysis, four twenty ml aliquots were taken; one from each of the four dilutions. In as much as the oxidation was to be made with periodate, two drops of phenolphthalein indicator was added to each and the acidity adjusted with 0.1 M hydrochloric acid to just colorless.

From here on, each aliquot was completed before the next was begun.

Ten ml of 0.2N periodate was added to the twenty ml aliquot, by means of a burette, and the reaction allowed to proceed for two hours. At this time the acidity was adjusted with 0.1 M sodium hydroxide to just pink to phenolphthalein. Twenty-five ml of saturated sodium bicarbonate and ten ml of twenty percent potassium iodide were added and the flasks swirled two to five minutes, till the liberation of iodine was complete. To decolorize the solution, ten ml of standard 0.2N arsenite was added from a burette and the excess arsenite titrated with 0.01124N iodine solution to a starch end point.

#1 Took 8.3 ml of 0.01124N I_2
2 9.7 ml
3 8.3 ml
4 9.1 ml

OXIDATION OF ALLYL ALCOHOL WITH PERMANGANATE-NO BARIUM ION

Aliquot	m.e. IO_4^-/250 used	g Allyl/250 Converted	g Allyl/250 Start	% Conversion
# 1	1.17	0.0170	0.0190	89.4
2	1.36	0.0196		104.0
3	1.17	0.0170		89.4
4	1.28	0.0185		97.5

Discussion

The ease of oxidation of the allyl alcohol double bonds to the corresponding saturated dihydroxy compound appeared to be considerably greater than that of crotonic and maleic acids.

This run made use of the manganate ion going to manganese dioxide step in the oxidation and the results, percent conversions, support the original hypothesis. Both the original oxidations and the analyses went smoothly but the reproducibility, between different dilutions, which were prepared under identical conditions, was poor. Here again, a reaction rate study would be very helpful.

The analyses were made using periodate because its specificity for α,β dihydroxy compounds is greater than that of perchlorato-cerate solution, and if the cerate method was used it was thought that the hydroxyl group of the unreacted allyl alcohol might be attacked.

A comparison of the results obtained by using the two different steps of neutral to slightly alkaline potassium permanganate oxidation to corresponding saturated dihydroxy compounds will be made after the following run.

Run #2

Again, four, ten ml samples of 0.0328M allyl alcohol were transferred, by means of a ten ml pipette, to two hundred ml Erlenmeyer flasks. To each of these flasks one gram of barium hydroxide and ten ml of a saturated solution of barium hydroxide were added, and the flasks swirled. From a graduated pipette, three ml of 0.1116M potassium permanganate was added to each of the four flasks. These quantities of allyl alcohol and potassium permanganate were approximately equi-molar. The solutions turned blue immediately and each flask was stoppered and placed on the shaker for four hours.

The precipitated barium manganate, and the excess undissolved barium hydroxide, was filtered off and then the four clear solutions were each treated with ten ml of saturated sodium carbonate solution to precipitate the excess barium ion in solution. Again the four solutions were filtered and then diluted to two hundred and fifty ml.

The analyses were carried out in an identical manner to the immediately preceding analyses.

#1 Took 4.1 ml of 0.01124N I_2
2 4.3 ml
3 5.3 ml
4 4.7 ml

OXIDATION OF ALLYL ALCOHOL WITH PERMANGANATE-BARIUM ION ADDED

Aliquot	**m.e. IO_4^-/250 used**	**g Allyl/250 Converted**	**g Allyl/250 Start**	**% Conversion**
# 1	0.576	0.008	0.019	44.0
2	0.605	0.009		46.2
3	0.745	0.011		56.8
4	0.660	0.010		50.5

COMPARISON OF ALLYL ALCOHOL CONVERSIONS

Titrating Agent	**No Barium**		**Barium**		**Titrating Agent**
	Aliquots	**% Conversion**	**Aliquots**	**% Conversion**	
	# 1	89.4	# 1	44.0	
I_2	2	104.0	2	46.2	I_2
	3	89.4	3	56.8	
	4	97.5	4	50.5	

Discussion

By comparing the percent conversions of both of the above allyl alcohol oxidations by potassium permanganate in neutral to slightly alkaline media a few facts may be brought out.

Although the percent conversions resulting from the oxidation where the reaction was stopped at the manganate ion were high, the differential between these and the percent conversions resulting from the oxidation where the reaction was allowed to proceed through the manganate ion to manganese dioxide is still in the order of two to one. The investigator felt that this large a differential was sufficient to warrant the statement that the results supported the original hypothesis.

CONCLUSIONS

1. The manganate ion, in alkaline solution, will oxidize crotonic and maleic acids to the corresponding saturated α,β dihydroxy compounds.

2. Neutral to slightly alkaline potassium permanganate oxidation of crotonic acid, maleic acid, and allyl alcohol to their corresponding saturated α,β dihydroxy compounds is essentially a step-wise reaction. The steps involved are: reduction of the permanganate ion to the manganate ion, and the reduction of the manganate ion to manganese dioxide.

3. In attempting to form corresponding saturated α,β dihydroxy compounds, by neutral to slightly alkaline potassium permanganate oxidation of crotonic acid and maleic acid, the first step of the above postulated step-wise reaction contributes little, if any, to the direct formation of these compounds.

4. The postulated step-wise reaction would support the theory of the formation of an intermediate complex between the double bonds of the reductant and the manganate ion, with its subsequent disproportionation to the corresponding saturated α,β dihydroxy compound.

5. The mechanism of neutral to slightly alkaline potassium permanganate oxidations of ethylenic type double bonds, to the corresponding saturated α,β dihydroxy compounds, proceeds predominantly by the step of manganate ion going to manganese dioxide, while the step of permanganate ion going to the manganate ion contributes little, if any, to this formation of corresponding saturated α,β dihydroxy compounds directly.

SUMMARY

The purpose of the investigation has been to make a study of the neutral to slightly alkaline potassium permanganate mechanism for the oxidation of ethylenic type double bonds to form the corresponding saturatedα,β dihydroxy compounds, especially with regard to crotonic acid, maleic acid and allyl alcohol.

The mechanism concerned with was,a step-wise reaction, such as; the first step in the oxidation was the permanganate ion going to the manganate ion; the second step in the oxidation was the manganate ion going to manganese dioxide, all during the oxidation of the organic compounds to their corresponding dihydroxy forms. The question then arose, which oxidation step accounted for the bulk of the dihydroxy compound formed.

To get away from using the unstable manganate ion directly for oxidation, a scheme of differentiation was devised. To limit an oxidation to only the first step, permanganate ion going to manganate ion, a saturated solution of barium ion, was added to the organic compound previous to the addition of permanganate. As far as manganate ion was formed, barium ion trapped it out of solution by precipitation as insoluble barium manganate. To bring out the action of the manganate ion in the oxidation to dihydroxy compounds, the reduction of the permanganate ion was allowed to proceed all the way to manganese dioxide, thus passing through the manganate ion step.

The percent conversions to the corresponding saturated α,βdihydroxy compounds, obtained by the above two methods, quite definitely showed that the oxidation proceeded predominantly by the step of manganate ion going to manganese dioxide and that the step of permanganate ion going to the manganate ion contributed little to the oxidation directly.

EXPERIMENTAL

B. POTASSIUM PERSULFATE

1. Preparation of reagents

(a.) 0.1N Potassium persulfate

The molecular weight of potassium persulfate is 270.31g and contains two equivalents per mole. Therefore it is 0.05 M in respect to the molecular weight.

By analytical balance, 13.5155g of the dry potassium persulfate was weighed out, dissolved in distilled water and diluted to one liter.

The investigator tried to standardize the potassium persulfate solution against standard base as outlined in Scott's Standard Methods of Analysis (7). The aqueous solution of the persulfate was decomposed by boiling according to the following equation:

$$2K_2S_2O_8 + 2H_2O \rightarrow 2K_2SO_4 + O_2 + 2H_2SO_4$$

The sulfuric acid formed in the fifteen minute hydrolysis was then titrated with standard 0.1N sodium hydroxide to a methyl orange end point. This method failed to give consistant results.

Experimentation brought out the fact that a blank, run in the same way as the oxidations except without the reductant, gave the most consistant results. In this method twenty-five ml of 6 M sodium hydroxide was added to a two hundred ml Erlenmeyer flask, twenty-five ml of the potassium persulfate was added from a burette, and then one-half gram of solid potassium iodide was added and the flask stoppered. The flask was then placed on a mechanical shaker for one hour, removed, and acidified with 6 M hydrochloric acid till the iodine color was permanent, two to five minutes. The liberated iodine was titrated to a starch end point with 0.1 N sodium thiosulfate.

$$S_2O_8^{=} + 2I^- \rightarrow 2SO_4^{=} + I_2$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

(b.) <u>0.2414M Ethyl alcohol</u>

A weighing bulb was blown from a soft glass test tube and absolute alcohol was added. The tube was sealed off and weighed, both before the alcohol was added and after. The tube was then broken beneath the surface of approximately seventy-five ml of distilled water and diluted to one hundred ml in a glass stoppered volumetric flask. The concentration of ethyl alcohol was 1.1122g per one hundred ml, from which the molarity was calculated.

(c.) <u>0.1860M Acetone</u>

The same procedure was used as in the preparation of the ethyl alcohol. The concentration of the acetone was 1.0806g per one hundred ml, from which the molarity was calculated.

(d.) <u>0.1M Phenol</u>

Weighed out 0.9411g of phenol analytically and dissolved in distilled water, diluting to one hundred ml.

(e.) <u>0.1M Crotonic acid</u>

Weighed out 2.0272 g of crotonic acid analytically and dissolved in distilled water, diluting to two hundred and fifty ml.

(f.) <u>0.1M Formaldehyde</u>

Used forty percent formalin solution to start with. The molecular weight of formaldehyde is 30.03g, so far a 0.1 M solution, $\frac{3.003}{.40}$g per liter was needed. For two hundred and fifty ml of a 0.1 M solution, 1.8769g of forty percent formalin was weighed out, dissolved in distilled water and diluted to two hundred and fifty ml.

2. Methods of calculation

All calculations on the potassium persulfate oxidations were made with the goal in view of determining the number of equivalents of persulfate reacting per mole of reductant. From these calculations it was then possible to postulate somewhat the end products of the oxidation as well as whether or not any oxidation had taken place.

The normality of the persulfate was calculated from the milliequivalents of thiosulfate used in the determination of the blank.

Determination of the number of equivalents of potassium persulfate used per mole of reductant:

$$\left[\begin{matrix}\text{(Blank titration)} \\ \text{(thiosulfate)}\end{matrix} - \begin{matrix}\text{(Run titration)} \\ \text{(thiosulfate)}\end{matrix}\right] \text{N thiosulfate} = \underset{\text{used}}{\text{m.e. of } K_2S_2O_8}$$

$$\frac{\text{m.e. } K_2S_2O_8}{\text{m.m. organic compound added}} = \frac{\text{e.} K_2S_2O_8}{\text{moles of organic compound}}$$

The results of each oxidation attempted, are listed and discussed after each experimental section.

An example of end product postulation:

In the case of formaldehyde the number of equivalents of persulfate per mole of formaldehyde was found to be approximately two.

$$\begin{array}{llll}
\text{Formaldehyde} = & H_2\ C\ O & \text{If goes to the acid} & H_2\ C\ O_2 \\
\text{HCHO} & +2\ 0\ -2 & & +2\ +2\ -4 \\
 & \multicolumn{3}{c}{\text{2 E} \longrightarrow} \\
 = & H_2\ C\ O & \text{If goes to } CO_2 & C\ O_2 \\
 & +2\ 0\ -2 & & +4\ -4 \\
 & \multicolumn{3}{c}{\text{4 E} \longrightarrow}
\end{array}$$

3. Procedures, calculated results, and discussion

(a.) Phenol

Two blanks were run by adding twenty-five ml of 6 M sodium hydroxide from a graduate, twenty-five ml of potassium persulfate and one-half gram of potassium iodide to two, two hundred ml Erlenmeyer flasks and placing them on a mechanical shaker for one hour. At the end of this time the solutions were diluted with fifty ml of water, to reduce the heating effect when the acid was added, and acidified with 6 M hydrochloric acid. The iodine liberated was titrated with 0.1042N sodium thiosulfate to a starch end point, and from this data, the normality of the potassium persulfate was calculated.

#1 Took 23.5 ml of 0.1042N $Na_2S_2O_3$

2 23.6 ml

To determine whether potassium persulfate would oxidize phenol, before a standard solution was made up, the investigator used a few crystals of solid phenol, swirled to dissolve, and then twenty-five ml of potassium persulfate was added from a burette. The flasks were stoppered and placed on the shaker for one hour, one-half gram of potassium iodide added and replaced on the shaker for ten minutes before acidifying with 6 M hydrochloric acid and titrating the liberated iodine with 0.1042N sodium thiosulfate.

#1 Took 2.4 ml of 0.1042N $Na_2S_2O_3$

2 7.2 ml

The difference between the blanks and these runs indicated that oxidation was taking place and would warrant the preparation of a standard solution of phenol to approach the problem from a more quantitative standpoint.

Run #1

Using twenty-five ml of 6 M sodium hydroxide and pipetting in one ml of 0.1 M phenol and then adding twenty-five ml of potassium persulfate should give fairly quantitative results. The flasks were stoppered and placed on the shaker for one-quarter hour, one-half gram of potassium iodide was added and the flasks replaced on the shaker for another one-quarter hour before acidifying with 6 M hydrochloric acid and titrating the iodine liberated, with 0.1042N thiosulfate.

#1 Took 16.5 ml of 0.1042N $Na_2S_2O_3$

2 17.1 ml

Run #2

Using the above procedure, only increasing the two shaking periods to one-half hour each, gave the following results.

#1 Took 17.25 ml of 0.1042N $Na_2S_2O_3$

2 17.4 ml

Run #3

Two shaking periods of three-quarters hours each.

#1 Took 16.0 ml of 0.1042N $Na_2S_2O_3$

2 16.0 ml

Run #4

Two shaking periods of one hour each

#1 Took 14.5 ml of 0.1042N $Na_2S_2O_3$

2 14.95 ml

Run #5

Two shaking periods of one and one-quarter hours each.

#1 Took 13.7 ml of 0.1042N $Na_2S_2O_3$

2 13.9 ml

OXIDATION OF PHENOL WITH POTASSIUM PERSULFATE

Run	m.e. $K_2S_2O_8$ used up	m.m. Phenol present	e. $K_2S_2O_8$ per mole phenol	Reaction Product
#1	0.691	0.100	6.91	

OXIDATION OF PHENOL WITH POTASSIUM PERSULFATE (Con't)

Run	m.e. $K_2S_2O_8$ used up	m.m. Phenol present	e. $K_2S_2O_8$ per mole phenol	Reaction Product
	0.633		6.33	
#2	0.618		6.18	Probably
	0.602		6.02	a mixture
#3	0.740		7.40	
	0.740		7.40	
#4	0.888		8.88	
	0.845		8.45	
#5	0.967		9.67	
	0.946		9.46	

Discussion

The attempts to standardize the potassium persulfate against standard 0.1075N sodium hydroxide failed, possibly due to incomplete hydrolysis upon boiling the solution for only fifteen minutes before the titration with standard base. Even when the potassium persulfate was allowed to react in the presence of an equal-volume of 2 M sodium hydroxide the hydrolysis appeared to be incomplete, giving rise to inconsistant titrations, with potassium iodide added, with sodium thiosulfate. By experimentation it was found that using equal volumes of 0.1N potassium persulfate and 6 M sodium hydroxide resulted in the most consistant results.

The order of addition of reagents, 6 M sodium hydroxide, reductant next and then potassium persulfate and allowing to react for one-half to one hour before the addition of potassium iodide, was determined by experimentation. It was also discovered that the liberation of iodine from the added potassium iodide by the excess persulfate was a slow process.

In strongly alkaline media:

$$S_2O_8^{=} + HOH \rightarrow SO_4^{=} + HSO_5^{-} + H^{+}$$

$$HSO_5^{-} + I^{-} \rightarrow SO_4^{=} + OI^{-} + H^{+}$$

$$3OI^{-} \rightleftharpoons IO_3^{-} + 2I^{-}$$

Upon acidification:

$$2OI^{-} + 4H^{+} \rightarrow I_2 + 2HOH$$

For this reason it was found necessary to allow the potassium iodide to remain in contact with the potassium persulfate for the same length of time as required for the original oxidation, before titrating the liberated iodine to determine the excess persulfate present.

The oxidation of phenol, which was apparent from the experimental data obtained, was as expected. Karrer (8) states that potassium persulfate, in the presence of silver sulfate, brings about an important decomposition of quinone to maleic acid and some fumaric acid. From this information it was not too difficult to see that the oxidation of phenol with potassium persulfate possibly resulted in a ruptured ring. From the investigators' experimental data it may be seen that the number of equivalents of persulfate used per mole of phenol, approached ten. There is little doubt that if the reaction was allowed sufficient time to go to completion, the number of equivalents of persulfate per mole of phenol would approach those of the theoretically calculated below.

If the phenol was oxidized to maleic and oxalic acids it would take fourteen equivalents.

$$H_6C_6O \rightarrow H_4C_4O_4 + H_2C_2O_4$$

phenol maleic oxalic

$$\begin{array}{ccccccc} H_6 & C_6 & O & \rightarrow & H_6 & C_6 & O_8 \\ +6 & -4 & -2 & & +6 & +10 & -16 \end{array}$$

$$\underbrace{-4 \qquad \xrightarrow{14\ e.} \qquad +10}$$

If the phenol was oxidized to maleic acid and carbon dioxide it would take sixteen equivalents

$$\begin{array}{lcll} H_6C_6O & \longrightarrow & H_4C_4O_4 & + \ 2CO_2 \\ \text{phenol} & & \text{maleic} & \text{carbon dioxide} \end{array}$$

$$\begin{array}{ccccccc} H_6 & C_6 & O & \longrightarrow & H_4 & C_6 & O_8 \\ +6 & -4 & -2 & & +4 & +12 & -16 \end{array}$$

$$\text{16 e.} \rightarrow$$

To explain the investigators' results, which are known to be low due to progressively different results upon extending the time of reaction, it should be realized that the purpose of this study was mainly to determine whether potassium persulfate would oxidize the different organic compounds tried, or not. With more emphasis on the conditions necessary to run a quantitative determination it would probably be possible to conclusively determine the end products of the reaction.

(b.) Crotonic and Maleic acids

In the crotonic acid run, two blanks were prepared in the same way as those used in the phenol runs and the titrations obtained were the same.

#1 Took 23.5 ml of 0.1042N $Na_2S_2O_3$

2 23.55 ml

Then for the attempted oxidation runs twenty-five ml of 6 M sodium hydroxide was added to two, two hundred ml Erlenmeyer flasks and one ml of 0.1 M crotonic acid was pipetted into each of the two flasks before adding twenty-five ml of potassium persulfate, stoppering and placing on the shaker for one hour. At the end of this time one-half gram of potassium iodide was added to each flask and the flasks were replaced on the shaker for another hour before acidifying with 6M hydrochloric acid and titrating the iodine liberated, with 0.1042N thiosulfate.

#1 Took 23.5 ml of 0.1042N $Na_2S_2O_3$

2 23.6 ml

These results didn't warrant varying the time of reaction.

The procedure used in the maleic acid runs was the same as that used in the crotonic acid runs above, only in this case one ml of 0.1 M maleic acid was used in place of one ml of 0.1 M crotonic acid.

#1 Took 23.4 ml of 0.1042N $Na_2S_2O_3$

2 23.5 ml

Again the results didn't warrant varying the time of reaction.

Discussion

The attempted oxidation of the double bonds of crotonic and maleic acids proved somewhat of a surprise to the investigator. The data indicated that the oxidizing power of potassium persulfate was not sufficiently large enough to attack ethylenic type double bonds under the conditions used.

(c.) Formaldehyde

To test the feasibility of preparing a standard formaldehyde solution the investigator made a run consisting of two samples of forty percent formalin. Twenty-five ml of 6 M sodium hydroxide was added to each of two flasks, one ml of forty percent formalin pipetted into each, and then twenty-five ml of potassium persulfate was added to each from a burette. The flasks were placed on the shaker for one hour, one-half gram of potassium iodide added to each and again shaken for one hour before acidifying with 6 M hydrochloric acid and titrating the iodine liberated, with 0.1042N thiosulfate.

#1 Took 0.05 ml of 0.1042N $Na_2S_2O_3$

2 0.05 ml

Two blanks were run at the same time, under the same conditions, and gave the following results.

#1 Took 21.75 ml of 0.1042N $Na_2S_2O_3$

2 21.80 ml

The differential between the blanks and the actual oxidation runs very definitely indicated oxidation of the formalin taking place. A standard solution of formaldehyde was then prepared as outlined under the section of this paper dealing with the preparation of reagents.

Run #1

Two blanks of twenty-five ml of 6 M sodium hydroxide, one-half gram of potassium iodide and twenty-five ml of potassium persulfate were shaken for one hour. After acidification with 6 M hydrochloric acid the liberated iodine was titrated with 0.1042N thiosulfate.

#1 Took 21.2 ml of 0.1042N $Na_2S_2O_3$

2 21.2

Two oxidations were run in the same manner as the blanks, with the exception that here one ml of 0.1 M formaldehyde solution was added, shaken one-half hour, one-half gram of potassium iodide added and the flasks replaced on the shaker for another one-half hour before acidifying and titrating the liberated iodine with thiosulfate.

#1 Took 18.9 ml of 0.1042N $Na_2S_2O_3$

2 18.9 ml

Two more oxidations were run, with the two shaking periods being one hour each instead of the above one-half hour periods.

#1 Took 19.1 ml of 0.1042N $Na_2S_2O_3$

2 19.2 ml

Run #2

When the amount of formaldehyde was increased from one to five ml of 0.1 M formaldehyde, while the rest of the constituents remained the same, and the shaking periods were one-half hour each, the following results were obtained.

#1 Took 11.6 ml of 0.1042N $Na_2S_2O_3$

2 11.65 ml

3 11.6 ml

4 11.4 ml

At the same time the blank remained the same 21.2 ml.

Run #3

Another series utilizing five ml of 0.1 M formaldehyde and one-half hour shaking periods was run, after preparing a new batch of potassium persulfate.

#1 Took 15.5 ml of 0.1042N $Na_2S_2O_3$

2 16.3 ml

3 16.1 ml

4 15.6 ml

The new blank determination was:

#1 Took 26.2 ml of 0.1042N $Na_2S_2O_3$

2 26.15 ml

Run #4

Another series utilizing both one and five ml of 0.1 M formaldehyde and two, one-half hour shaking periods was run. The first two samples contained one ml of 0.1 M formaldehyde and the results were:

#1 Took 23.45 ml of 0.1042N $Na_2S_2O_3$

2 23.50

The second two samples contained five ml of 0.1 M formaldehyde and the quantity of potassium persulfate used was increased to fifty ml from the previously used twenty-five.

#3 Took 38.35 ml of 0.1042N $Na_2S_2O_3$

4 40.30 ml

The new blank determination was:

#1 Took 25.4 ml of 0.1042N $Na_2S_2O_3$

2 25.4 ml

Run #5

As a conclusion to the formaldehyde oxidations the investigator reverted back to the small formaldehyde concentration of one ml of a 0.1 M solution. The blanks, #1 and 2, contained twenty-five ml of 6 M sodium hydroxide, twenty-five ml of potassium persulfate and one-half gram of potassium iodide, and were placed on the shaker for one hour before acidifying with 6 M hydrochloric acid and titrating the iodine liberated, with 0.1042N thiosulfate. The samples, #3, 4, 5, and 6, had in addition, one ml of 0.1 M formaldehyde and were shaken for two one-half hour periods.

#1 Took 25.5 ml of 0.1042N $Na_2S_2O_3$

2 25.4 ml

3 23.6 ml

4 23.5 ml

5 23.6 ml

6 23.8 ml

OXIDATION OF FORMALDEHYDE WITH POTASSIUM PERSULFATE

Run	m.e. $K_2S_2O_8$ used up	m.m. Formaldehyde Present	e. $K_2S_2O_8$ per mole formaldehyde	Reaction Product
#1	0.204	0.10	2.04	
	0.204		2.04	Formic

OXIDATION OF FORMALDEHYDE WITH POTASSIUM PERSULFATE (Con't)

Run	m.e. $K_2S_2O_8$ used up	m.m. Formaldehyde Present	e. $K_2S_2O_8$ per mole formaldehyde	Reaction Product
	0.186		1.86	acid
	0.177		1.77	
#2	9.850	0.50	1.70	Formic acid
	0.845		1.69	
	0.840		1.68	
	0.870		1.74	
#3	1.160	0.50	2.32	?Mixture Formic acid and possibly Carbon dioxide
	1.075		2.15	
	1.095		2.19	
	1.150		2.30	
#4	0.207	0.10	2.07	Formic acid
	0.202		2.02	
	1.320	0.50	2.64	?Mixture
	1.115		2.23	
#5	0.191	0.10	1.91	Formic acid
	0.202		2.02	
	0.191		1.91	
	0.170		1.70	

Discussion

Formaldehyde oxidation presents a promising quantitative procedure. The concentration of formaldehyde must however be low and a large excess of potassium persulfate must be present to give a satisfactory period of reaction and still obtain complete oxidation. From the investigators' experimental data it was apparent that persulfate will only take the aldehyde to the corresponding acid, and not all the way to carbon dioxide, if the reactants are used in the proper proportion.

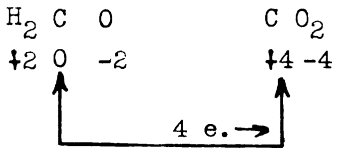
From looking at the tabulated data it can be seen that when the concentration of formaldehyde was increased from 0.1 millimoles to 0.5 millimoles the resulting oxidation products were possibly mixtures, especially when the concentration of potassium persulfate used was doubled. The investigator concluded however, that in as much as the increase in equivalents of potassium persulfate required per mole of formaldehyde was just slightly over the two required to obtain formic acid as a reaction product, that this difference was possibly due to experimental error.

To test this fact the investigator planned to try oxidizing oxalic acid with potassium persulfate.

The method by which the investigator arrived at the postulated reaction products was as follows.

From the data it was found that two equivalents of potassium persulfate were required per mole of formaldehyde.

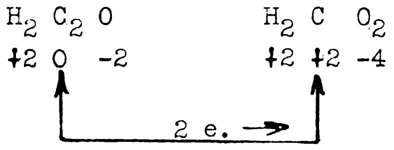
To go to carbon dioxide would take,



$$\begin{array}{ccc} H_2 & C & O \\ +2 & 0 & -2 \end{array} \qquad \begin{array}{cc} C & O_2 \\ +4 & -4 \end{array}$$

4 e. →

To go to formic acid would take,



$$\begin{array}{ccc} H_2 & C_2 & O \\ +2 & 0 & -2 \end{array} \qquad \begin{array}{ccc} H_2 & C & O_2 \\ +2 & +2 & -4 \end{array}$$

2 e. →

(d.) <u>Oxalic acid</u>

The blanks were determined and found to be:

#1 Took 25.4 ml of 0.1042N $Na_2S_2O_3$

2 25.5 ml

Six oxidation runs were made by placing twenty-five ml of 6 M sodium hydroxide, one ml of 0.1 M (0.05N) oxalic acid and twenty-five ml of potassium persulfate in two hundred ml Erlenmeyer flasks, shaking for one-half hour, adding one-half gram of potassium iodide and shaking for another one-half hour before acidifying with 6 M hydrochloric acid and titrating the liberated iodine with 0.1042 sodium thiosulfate.

#1 Took 25.45 ml of 0.1042N $Na_2S_2O_3$

2 25.45 ml

3 25.50 ml

4 25.60 ml

5 25.40 ml

6 25.60 ml

Discussion

The data obtained indicates that potassium persulfate does not attack carboxyl groups or split carbon to carbon bonds, when these carbon atoms do not have glycol type structure. There was no evidence of evolved carbon dioxide, the expected decomposition product of oxalic acid, when it was oxidized.

(e.) **Ethyl alcohol**

The blanks were run in the same manner as previously, with the addition of one-half gram of potassium iodide at the same time as the potassium persulfate and shaking for one hour.

#1 Took 40.5 ml of 0.1042N $Na_2S_2O_3$

2 40.4 ml

Two runs of the blank constituents, plus one ml of 0.2414M ethyl alcohol, were made with two one-half hour shaking periods.

#3 Took 22.75 ml of 0.1042N $Na_2S_2O_3$

4 32.70 ml

Four runs of the blank constituents, plus one ml of 0.2414M ethyl alcohol, were made with two one hour shaking periods.

#5 Took 22.2 ml of 0.1042N $Na_2S_2O_3$

6 36.2 ml

7 36.9 ml

8 37.8 ml

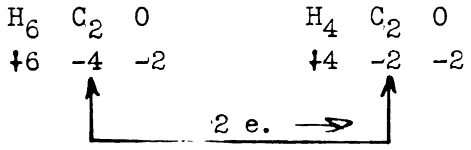
OXIDATION OF ETHYL ALCOHOL WITH POTASSIUM PERSULFATE

Run	m.e. $K_2S_2O_8$ used up	m.m. Ethyl alcohol present	e. $K_2S_2O_8$ per mole alcohol	Reaction Product
#3	2.980	0.2414	12.39	Ranges primarily
4	1.308		5.42	from acetaldehyde
5	3.080		12.75	to acetic acid
6	0.720		2.98	a mixture
7	0.600		2.49	
8	0.447		1.85	

Discussion

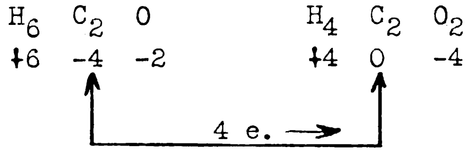
The experimental data on ethyl alcohol oxidation led the investigator to believe that the end products of the oxidation were acetaldehyde, acetic acid, or a mixture of these, depending on the reaction time used.

If the ethyl alcohol went to the aldehyde, two equivalents of potassium persulfate would be used up per mole of alcohol.



ethyl alcohol acetaldehyde

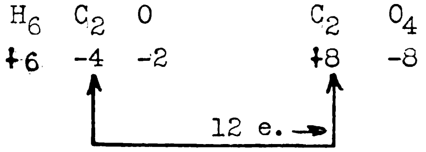
If the alcohol went to the acid, four equivalents of potassium persulfate would be used up per mole of alcohol.



ethyl alcohol acetic acid

By extending the reaction time to say two to four hours, instead of the one hour that the investigator used, it might be possible to take the alcohol to acetic acid in quantitative amounts.

Runs #3, 4 and 5 appeared to have been incomplete, in that they indicated side reactions or faulty technique, because to use twelve equivalents of potassium persulfate per mole of ethyl alcohol the alcohol would have to go to carbon dioxide.



These oxidations were made at the shorter reaction time, two, one-half hour periods, which also contributed to the investigator's belief that a side reaction had taken place or the technique used was faulty. It had also been proved that potassium persulfate would not attack the carboxyl radical, in the cases of crotonic, maleic, and oxalic acids. Even the much stronger potassium permanganate oxidation did not attack further acetic acid if it was one of the products formed.

Another explanation of the results obtained in #3, 4 and 5 oxidations, and possibly a more satisfactory one, would be the formation of iodoform by the reaction of the acetaldehyde formed and the hypoiodite ion present in the strongly alkaline solution.

(f.) Acetone

The blanks, and the acetone oxidations, employed the same procedures as were used in the ethyl alcohol oxidations. The acetone used was 0.1860M.

Blanks of one, one hour shaking period.

#1 Took 39.40 ml of 0.1042N $Na_2S_2O_3$
2 39.10 ml

Two, one-half hour shaking periods-oxidation.

#3 Took 26.45 ml of 0.1042N $Na_2S_2O_3$
4 27.20 ml

Two, one hour shaking periods-oxidation.

#5 Took 27.90 ml of 0.1042N $Na_2S_2O_3$
6 28.20 ml
7 28.40 ml
8 28.40 ml

A light yellow precipitate was formed soon after the addition of the potassium iodide, which remained throughout the acidification and sodium thiosulfate titration.

OXIDATION OF ACETONE WITH POTASSIUM PERSULFATE

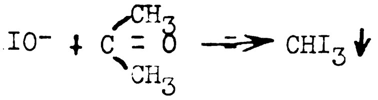
Run	**m.e. $K_2S_2O_8$ used up**	**m.m. Acetone present**	**e. $K_2S_2O_8$ per mole acetone**	**Reaction Product**
#3	2.13	0.1860	11.45	
4	2.00		10.76	Unpredictable due to formation of iodoform
5	1.89		10.15	
6	1.84		9.90	
7	1.81		9.71	
8	1.81		9.71	

Discussion

There was little doubt that the acetone was oxidized to some extent by the potassium persulfate but no predictions could be made as to the end products because under the conditions used, iodoform was precipitated. Iodide ion, in the presence of an oxidizing agent and strongly alkaline media, forms hypoiodite, which with acetone, gives a precipitate of iodoform.

$$S_2O_8^{=} + I^- \longrightarrow I_2 + SO_4^{=}$$

$$I_2 + OH^- \longrightarrow IO^- + H^+ + I^-$$



$$IO^- + (CH_3)_2C = O \longrightarrow CHI_3\downarrow$$

As a suggestion for further study the investigator would like to see other ketones used, in the same manner as the acetone was, with a different means of back-titration of the excess persulfate.

(g.) 3, 4 Butanediol

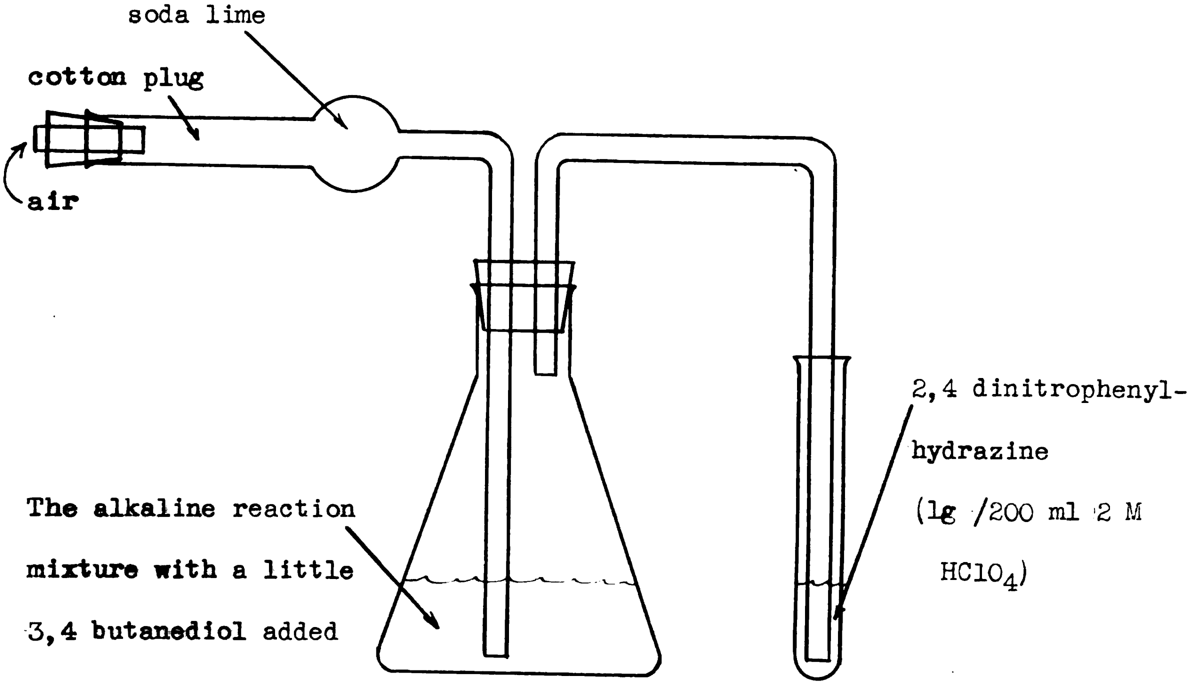
The 3, 4 butanediol was used in an attempt to determine just what the potassium persulfate did to the potassium iodide which was added.

The investigator weighed out two potassium iodide samples to 0.05g ± 10g into two, three hundred ml Erlenmeyer flasks. To numbers 1 and 2 was added twenty-five ml of 6 M sodium hydroxide and twenty-five ml of potassium persulfate, stoppered and placed on the shaker for four hours.

In a third flask, only twenty-five ml of 6 M sodium hydroxide and twenty-five ml of potassium persulfate was added, stoppered and shaken for four hours.

At the end of the four hour shaking periods a little (5-10 ml) 3, 4 butanediol was added to each of the three flasks and a stream of air was bubbled through the solutions, sweeping the volatile products of the oxidation over into test tubes containing a perchloric acid solution of

2, 4 dinitrophenylhydrazine.



Flask #1

The reaction was very slow, with no precipitate formed by the time the other flasks had. Upon the addition of more glycol the precipitate began to form.

The melting point of the impure precipitate was 115°-124°C.

Flask #2

The reaction solution was a light yellow color with some cloudiness while the phenylhydrazine filled tube contained a rich orange precipitate.

The melting point of the impure precipitate was 89°-110°C.

Flask #3- no iodide added

The reaction solution was a deep yellow color and clear while the phenylhydrazine filled tube contained a rich orange precipitate.

The melting point of the impure precipitate was 106°-108°C.

The melting points of some of the 2, 4 dinitrophenylhydrazones are listed below.

Formaldehyde derivative	166°C
Acetaldehyde	147°
	168°
Propionaldehyde	154°
n-Butyraldehyde	122°
n-Heptaldehyde	108°

As can be seen from comparing the above melting points with those obtained in the three runs on 3, 4 butanediol just completed, the derivatives obtained were of a complex mixture and little can be deduced other than that the reaction products of potassium persulfate oxidation of 3, 4 butanediol contain aldehydes.

As a check on the procedure the investigator ran three more samples, exactly the same as previously, up to the point where they were removed from the shaker.

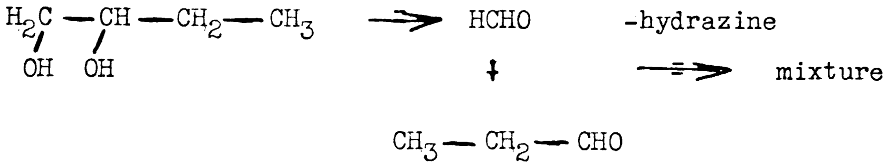
After three hours of shaking, the flasks were removed and neutralized to a phenolphthalein end point with 6 M hydrochloric acid. Then 3, 4 butanediol was added to each of the three flasks and air bubbled through, over into the 2, 4 dinitrophenylhydrazine solution.

At the end of one and one-half hours there was no precipitate formed in any one of the three test tubes, only a slight coloring of the reaction mixtures in #1 and 2, while the blank, #3, was perfectly colorless.

Discussion

As much as the primary end products of splitting a glycol with periodate are aldehydes and most aldehydes give a precipitate with 2, 4 dinitrophenylhydrazine, the investigator selected this means for determining whether potassium persulfate oxidized glycols by splitting and possibly what the oxidation products are.

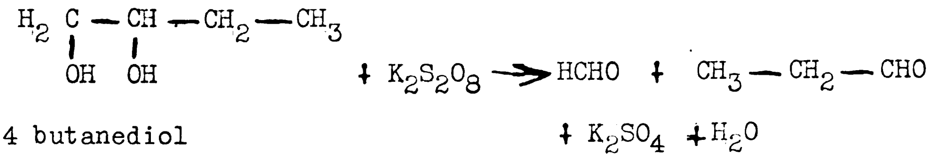
The phenylhydrazine precipitates showed that persulfate readily splits 1, 2 glycols but unfortunately, the melting points of the precipitates weren't of much use in identification due to the fact that they were impure and in quantities that didn't allow extensive purification. The precipitates were also composed of two different components, thus:



$$\underset{OH}{H_2C}-\underset{OH}{CH}-CH_2-CH_3 \longrightarrow \begin{matrix} HCHO \\ + \\ CH_3-CH_2-CHO \end{matrix} \xrightarrow{\text{-hydrazine}} \text{mixture}$$

Another point brought out by the experimental data was that, a reiteration of previous findings, the oxidation of 1, 2 glycols with potassium persulfate must be carried out in very strongly alkaline media. This was shown by comparing the results of the first three samples, in alkaline media, with those of the second three samples, in neutral media. In neutral media no phenylhydrazine precipitate was formed, indicating no splitting of the glycol added.

Another purpose of the 3, 4 butanediol oxidation was to attempt to determine whether or not the potassium persulfate oxidizes the iodide ion to the periodate ion, which then in turn splits the glycol, or whether the potassium persulfate directly splits it. In as much as the sample containing no iodide ion appeared to result in more phenylhydrazine precipitate, smaller melting point range and faster than the ones which contained iodide ion, the investigator believed that the splitting of the glycol was a direct process. Possibly the reaction is:



$$\underset{OH}{H_2C}-\underset{OH}{CH}-CH_2-CH_3 + K_2S_2O_8 \longrightarrow HCHO + CH_3-CH_2-CHO + K_2SO_4 + H_2O$$

3, 4 butanediol

CONCLUSIONS

1. For the most satisfactory oxidation of organic compounds to take place with potassium persulfate it should take place in strongly alkaline medium.

2. Potassium persulfate does not attack ethylenic type bonds to any appreciable extent under strongly alkaline conditions.

3. Potassium persulfate does not attack carboxyl groups to any appreciable extent under strongly alkaline conditions. That is, an oxidation is stopped at the carboxyl product under these conditions.

4. Potassium persulfate oxidizes phenols in strongly alkaline medium but the end products are uncertain due to incomplete reaction.

5. Potassium persulfate oxidized formaldehyde to formic acid, when based on equivalents of persulfate used per mole of formaldehyde, in strongly alkaline medium.

6. It is indicated that potassium persulfate oxidizes ethyl alcohol to yield a mixture of the aldehyde and the acid in strongly alkaline medium and might be made quantitative to the acid by lengthening the reaction time.

7. It is indicated that potassium persulfate oxidizes acetone in strongly alkaline medium but a different means of titration of excess persulfate must be used than the iodometric procedure used by the investigator.

8. No conclusive evidence was found to show that the persulfate oxidation is an indirect one in which the persulfate first oxidizes the iodide ion to the periodate ion, which in turn does the oxidizing.

9. It is indicated that potassium persulfate readily splits 1, 2 glycols in strongly alkaline medium to give primarily aldehydes.

10. It is best to keep the concentration of reductant small and the concentration of persulfate high in all the oxidations.

SUMMARY

The purpose of the investigation was to make a study of just what types of organic compounds were oxidized, if at all, by potassium persulfate in strongly alkaline media, and an attempt was made to determine what the reaction end products might be.

The compounds studied were phenol, crotonic and maleic acids, formaldehyde, oxalic acid, ethyl alcohol, acetone and 3, 4 butanediol.

The procedure employed in the study was to dissolve 0.1 millimoles of the organic compound in excess 6 M alkali and then add a measured excess of potassium persulfate. The reaction time was varied from one-quarter hour to one and one-quarter hours. At the end of this reaction time an excess of potassium iodide was added and the same length of time allowed for this reaction as was allowed in the organic oxidation. The solution was then acidified with 6 M hydrochloric acid and the liberated iodine titrated with standard thiosulfate. A blank was run in each case to find the normality of the persulfate and to use in determining the equivalents of persulfate consumed in the oxidation of the organic compound.

Results obtained indicated the persulfate could be used as a mild oxidizing agent for some organic compounds, when in strongly alkaline solution and within proper limits of concentration.

Some of the most promising results were obtained with phenol, formaldehyde and ethyl alcohol. Little attack on double bonds (ethylenic type) or carboxyl groups was indicated under the conditions used.

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