AN ABSTRACT OF THE THESIS OF

(Name) (Name) (Majer)

Date Thesis presented ____ March_31._1938

Title___ The Selective Oxidation of Organic Compounds

Particularly by Todic Acid.

Redacted for privacy

Abstract Approved:

(Major Professor)

- 1. Seven oxidizing solutions were used in the study of the partial oxidation of organic compounds. The extent of oxidation of different compounds was determined by titration of the unused amount of reagent. The number of equivalents of oxygen consumed per mol in relation to the number of equivalents necessary for complete oxidation was used as a basis of comparison. From the data thus obtained the end products were postulated and the specificity as to organic groups, if any, noted.
- 2. The results obtained by use of potassium permanganate, potassium dichromate, and ceric sulphate solutions under the various conditions tried showed they were not specific, but exhibited lendency to oxidize the compounds completely.
- 3. In the case of iodic acid a marked selectivity was noticed. Certain types of compounds such as alighatic alcohols, with the exception of methanol, aldehydes and ketones, were oxidized. Aldohexoses and most polyhydric alcohols were unattacked. The extent of the selectivity is better obtained by examinat of Table VI.
- Former work using periodic acid solutions under oxidizing conditions was extended to include the hydroxy butyric acids.

THE SELECTIVE OXIDATION OF ORGANIC COMPOUNDS PARTICULARLY BY IODIC ACID

by

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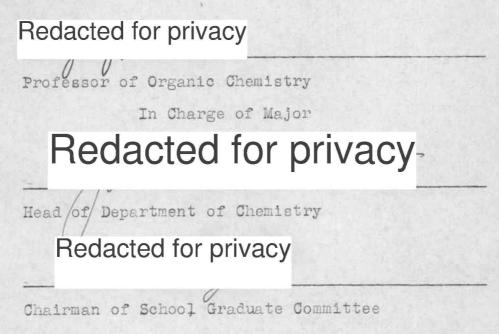
A THESIS submitted to the OREGON STATE COLLEGE

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

June 1938

APPROVED:



Redacted for privacy

Chairman of State College Graduate Council

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THE SELECTIVE OXIDATION OF ORGANIC COMPOUNDS PARTICULARLY BY IODIC ACID

Introduction

Most of the work in the field of oxidation of organic compounds has been centered on the problem of the character of the end products formed. Until recent years, (4, 8, 11, 12, 13, 17, 18, 19) comparatively little attention has been paid to the amount of oxidizing agent actually consumed in the oxidation process.

In this study a series of known pure compounds was submitted to oxidizing conditions and the amount of oxidant consumed in each case was determined by back titration. The number of equivalents of oxygen consumed per mol of substance was calculated and the result compared with the number of equivalents of oxygen per mol of substance had the reaction gone to completion. By these comparisons it was hoped that in the case of some of the reagents, at least, the end products could be postulated and that the groups present in the original compound might be made determinable in this manner. This would constitute a new tool with which to probe molecular structure.

Hydroxy compounds were selected for study with the hope that some of this work would be useful in studying the structure of "pantothenic acid" which is known to be a hydroxy compound.

In order that this approach to organic oxidations be of value the reagents should be used under circumstances which will allow the residual amount of oxidizing reagent present at any time to be determined by simple means. Also the conditions chosen should be that the maximum amount of selectivity, as to types of compounds or organic groups attacked, be snown by the reagent under observation.

The results obtained in the case of iodic acid (9, 11, 12, 19) give evidence that at least one reagent has been found that is useful. In the other cases no useful degree of selectivity has been demonstrated under the conditions used.

Other reagents investigated included a. Potassium permanganate in $3\frac{1}{2}$ per cent sodium carbonate solution (5, 7, 15). b. Potassium permanganate in dilute sodium hydroxide solution, used in the cold (7, 10). c. Potassium permanganate in neutral solution (10). d. Potassium dichromate in glacial acetic acid solution (3, 5). e. Potassium iodate in glacial acetic acid solution. f. Ceric sulphate in dilute sulphuric acid solution (20). g. Potassium periodate in dilute sulphuric acid solution.

Preliminary experiments were run on each of the above reagents to see whether or not they appeared promising. If unpromising results were obtained, other reagents were

studied in turn.

No work was attempted using such reagents as lead tetra-acetate (6), peracetic acid (2), iodo-silver benzoate (14), selenium dioxide (1), or osmium tetraoxide and hydrogen perioxide, or chlorates (13).

Experimental Procedure

Since it was the object to secure partial oxidation, the conditions used were milder than those necessary for complete oxidation. All reactions were carried out, unless otherwise stated, in ordinary six-inch test tubes which were placed in a constant level water bath and maintained at the boiling temperature of water. All glassware was previously cleaned with hot chromic-sulphuric acid cleaning solution to prevent possible contamination.

Potassium Permanganate in <u>3</u>¹/₂ Per Cent Sodium Carbonate Solution.

Five milligram samples of the compounds to be oxidized were weighed directly into the test tubes, 10 ml of 2.4 N potassium permanganate dissolved in $3\frac{1}{2}$ per cent sodium carbonate solution added, the whole shaken and placed in a water bath. After $1\frac{1}{2}$ hours the reaction mixtures were rinsed into 250 ml erlenmeyer flasks with distilled water. The contents were then neutralized with 50 ml of 1 per cent sulphuric acid and the excess permanganate destroyed with a weighed quantity of standardized ferrous ammonium sulphate. The amount of permanganate not used in oxidizing the compound was determined by diluting the volume to 100 ml and back-titrating with 0.1 N potassium permanganate in the presence of 5 ml of 85 per cent

ortho-phosphoric acid.

TABLE I

Results of Oxidations with Potassium Permanganate in 3¹/₂ Per Cent Sodium Carbonate Solution After 1¹/₂ Hours

Compound	Experimental number: Theoretical Number of milliliters of : for Oxidation N Oxidant per milli-: mol of substance :					
Mandelic Acid : Glycollic Acid : Tartaric Acid :	3.69 4.47 8.9	4.0 for side chains 6.0 complete 10.0 complete				
Meta-hydroxy- : benzoic Acid : Nicotinic Acid : 2,6 dimethyl 4 : hydroxy Ethyl :	23.2 5.8	28.0 complete 22.0				
Nicotinic Acid: 2,6 dimethyl 4 :	23.6	:24.0 for side chains				
hydroxy Nico-: tinic Acid : Blank :	6.0 0.0	32.0 complete				

All compounds tried in these preliminary experiments were attacked, but as no apparent specificity as to other groups or types of compounds, except for the oxidations of the side chains in the cases of mandelic acid and 2,6 dimethyl, 4 hydroxy ethyl nicotinic acid, was discovered, no further investigation was attempted.

Potassium Permanganate in Cold Alkaline Solution.

Earlier work, as referred to by I. M. Koltholf (7) suggested the feasibility of using cold potassium permanganate solution as an oxidant. Different types of compounds other than those referred to previously were tried.

Five milligram samples were introduced into 100 ml ground glass-stoppered flasks, followed by the addition of 25 ml of 0.123 N potassium permanganate and 10 ml of 4 N sodium hydroxide. The solutions were placed in a dark cabinet for 24 hours at room temperature. At the end of this period the mixtures were neutralized with 4 N sulphuric acid solution and diluted to 100 ml. The remaining permanganate was reduced with $l_{\rm E}^{1}$ grams of Mohr's salt. The excess of Mohr's salt present was determined by titration with 0.1 N permanganate in the presence of 5 ml of 85 per cent ortho-phosphoric acid.

TABLE II

Results	01	Usir	ng Potassi	lum Permanganate
	in	Cold	Alkaline	Solution

Compound	:Experimental n :of milliliters :N Oxidant per :mol of substan	of : milli-:	for Complet	
After 24 hours				
B-Alanine l-Theonine B-Amino Butyric	11.65 9.55		12.0 16.0	
Acid , B dihydroxy-	10.60		18.0	
Butyric Acid	8.68		16.0	
(Calcium Salt)			12.0	
Acetic Acid Acetone	0.0 10.73		8.0 16.0	
After 50 hours				
Lactic Acid	: 10.0	:	12.0	

In some cases, such as exemplified by B-amino butyric acid, the number of equivalents of oxygen which would be consumed had the reaction gone to completion, minus the experimental value obtained, gave a difference numberically equal to the number of equivalents of oxygen which would be necessary to oxidize acetic acid to completion. This would suggest that one of the end products of the reaction would be acetic acid. However this could not be shown to be the general case for at the same time no specificity for attacking any one type of compound or groups could be demonstrated.

Potassium Permanganate in Neutral Solution.

In the following reactions the permanganate solutions, which in the above experiments become alkaline as the reaction proceeds, were kept neutral by the presence of magnesium sulphate which precipitates the hydroxyl ion as fast as it is formed.

Five milligram samples were placed in test tubes with 3 ml of 0.6 N potassium permanganate, 7 ml of water and 1 gram of solid magnesium sulphate. This mixture was placed in a water bath for $1\frac{1}{2}$ hours. At the end of this time the solution was acidified, Mohr's salt added, and the excess titrated as before in the presence of orthophosphoric acid.

TABLE III

Results Obtained by Using Potassium Permanganate in Neutral Solution After 12 Hours

Compound	:Experimental Number :of milliliters of :N Oxidant per milli :mol of substance	
	9.5 6.1 10.06	4.0 for side chains 6.4 complete 10.0 complete
Benzoic Acid Citrazinic Acid Nicotinic Acid 2,4 dimethyl 6	18.2 7.0	28.0 complete 18.0 complete 22.0 complete
hydroxy Ethyl Nicotinic Acid Blank		24.0 for side chains

Although neutral permanganate solutions gave results showing more nearly complete oxidation than in the case of alkaline permanganate, sufficient selectivity was not evidenced in any of the experiments to make it seem desirable to extend the study further.

Potassium Permanganate in Glacial Acetic Acid Solution.

In view of the fact that acetic acid is not attacked by potassium permanganate solutions, this mixture was tried under the same general conditions of temperature and time of oxidation as used in the other experiments with permanganate. However, back titration and comparing with blanks showed that the permanganate underwent excessive decomposition in this type of solution.

Potassium Dichromate in Glacial Acetic Acid.

Five to six milligram samples were placed in test tubes containing 2 ml of normal potassium dichromate plus 10 ml of glacial acetic acid. At the end of the reaction time the solution was further acidified with hydrochloric acid, diluted to approximately 150 ml, 0.75 grams of sodium bicarbonate added (to give an atmosphere of carbon dioxide) plus 1¹/₂ grams of potassium iodide. The iodine liberated by the excess dichromate present was titrated with 05 N sodium thiosulphate solution using starch indicator.

TABLE IV

Results of the Experiments Using Potassium Dichromate in Glacial Acetic Acid as an Oxidizing Agent

Compounds	:Samp	le:o gs:O	xpt'l Numbe f ml of N widant per ubstance	r: :Theoretical Num- : ber for Oxida- : tion		
After 12 hours.						
Mandelic Acid Glycollic Acid Tartaric Acid Meta-Hydroxy- Benzoic Acid Blank	· 5.0 · 55.0	:	2.24 3.96 10.0 11.8 0.0	: 6.0 :10.0	for side complete complete	chains
After 2 hours. Mandelic Acid Glycollic Acid Tartaric Acid Meta-Hydroxy- Benzoic Acid Blank	5.00 5.00 5.00		6.55 6.63 10.2 16.6 0.0	: 6.0 :10.0	for side complete complete complete	chains

The gradual increase in consumption of oxidizing agent with the time as shown in most cases indicated that the reagent was not specific but generally attacked all compounds, the extent of which was dependent upon the time allowed for the reaction.

Potassium Iodate in Glacial Acetic Acid Solution.

The mixtures containing potassium icdate in the presence of excess glacial acetic acid proved unsatisfactory owing to the fact that reduction was shown in the blank. This indicated that the acetic acid was being slightly oxidized.

Ceric Sulphate in Dilute Sulphuric Acid.

An approximately 0.1 N solution of ceric sulphate in 10 per cent sulphuric acid was standardized against sodium oxalate (15). Ten ml of this solution together with the sample were introduced into test tubës which were placed in a boiling water bath. At the end of 1¹/₂ hours the contents of the test tubes were rinsed into 400 ml beakers with distilled water. The solutions were diluted to approximately 150 ml, and 20 ml of exactly 0.1 N sodium oxalate added. The solutions were heated nearly to boiling and the excess oxalate determined by titration with .06 N ceric sulphate solution. The yellow coloration in hot solutions was used as an indicator.

TABLE V

Compound	:Sample in mgs		: Theoretical Num- : ber for Complete
Mandelic Acid Glycollic Acid	: 5.0	5.92.	3 ¹ .0
Tartaric Acid Meta-Hydroxy-	: 5.0		10.0
Benzoic Acid 2,4 dimethyl Ethyl Nicotin-	:	7.13	28.0
ic Acid 2,3 dimethyl 4 hydroxy	4.4	17.8	44.0
Nicotinic Acid Cinchomeric Acid Blank		7.4 8.55 0.0	32.0 22.0

Results Obtained Using Ceric Sulphate After $l\frac{1}{2}$ Hours

In all cases tried the reagent did not evidence any selectivity, but attacked all compounds with apparently no definite stopping point.

The reagent was therefore not investigated further.

Potassium Iodate in 40 Per Cent Sulphuric Acid.

Five milligram samples were introduced into test tubes together with a mixture consisting of 10 ml of 1 per cent potassium iodate in 40 per cent sulphuric acid and 2 ml of water. Each was then placed in a water bath and kept at the boiling temperature of water. At the end of the reaction time the mixture was rinsed into 250 ml erlenmeyer flasks with distilled water and the whole diluted to approximately 100 ml. The iodine liberated during the reaction was volatilized by boiling the solution for 5 minutes. Sodium bicarbonate (0.75 gram) was added to give an atmosphere of carbon dioxide and 1.5 grams of potassium iodide. The iodine liberated by the excess iodic acid present was titrated with 0.05 N sodium thiosulphate using starch indicator.

In case no visible liberation of iodine occurred it was found unnecessary to titrate because such titrations uniformly yielded results comparable with blanks.

In experiments where the oxidation of the compound was very slight or the sample used was very small, the liberated iodine was extracted with chloroform and a subsequent comparison made with a standard iodine in chloroform solution, in the colorimeter. This method proved extremely sensitive and gave very satisfactory estimates of the amount of oxidant used.

The reactions were carried out in ordinary six-inch test tubes which were sealed by fusing. At the end of the reaction time the seals were broken and the reaction mixture was quickly rinsed into a small separatory funnel with distilled water. Four extractions were made with 6 ml of chloroform. The final volume was made up to 25 ml before comparison with the standard.

The standard solution for comparison was prepared by allowing 10 ml of 0.001 N potassium iodate solution to react with excess potassium iodide, followed by immediate extraction with chloroform and dilution to volume like with the unknown. Evaporation of both standard solution and the sample was prevented by covering the chloroform extractions with a layer of water. For results see Table VI-b.

The period of time originally allowed for the oxidation was $l_2^{\frac{1}{2}}$ hours but later trials showed that satisfactory results could be obtained in a much shorter period of time.

Experiments were performed under a strong light as well as in the dark. The results of the latter showed that light not only promoted the reaction, but that it also goes further toward completion.

TABLE VI-A

Results Obtained Using Potassium Iodate in 40 Per Cent Sulphuric Acid Mixtures Reaction Time 1¹/₂ hours

	the second second	And the second second	
Compound	:Sample: :in mgs:	Expt'l Numbe: of ml of N Oxidant per millimol of Substance	r: :Theoretical Num- : ber for Complete : Oxidation
Methanol N Propyl Alcohol 2° Amyl Alcohol N Hexy Alcohol N Hepty Alcohol N Octyl Alcohol	7.98 8.0 8.2 8.2 8.3 8.4	0.0 10.3 17.15 9.37 3.11 14.75	6.0 18.0 34.0 38.0 42.0 48.0
Ethylene Glycol Glycerol Erythritol Pentaerythritol Sorbitol Ducitol Adonitol Mannitol Eri Nothylene	73749406	0.0 0.0 0.0 0.0 0.0 0.0 0.0	10.0 14.0 18.0 72.0 26.0 26.0 26.0 26.0
Tri Methylene Glycol Pinacol Hydrate	10.5	5.66 4.2	16.0 34.0
Acetaldehyde Propionaldehyde Butyraldehyde Formaldehyde Benzaldehyde	\$.0 8.7 8.2 10.5	4.91 9.82 16.60 .39 4.43	10.0 16.0 22.0 4.0 32.0
Acetone	7.92	12.4	24.0
Methyl Ethyl Ketone Michler's Ketone Acetophenone	5.0 5.7 10.3	13.45 35.4 5.13	22.0 108.0 38.0
Benzil Benzophenone	4.4 5.2	0.0	62.0 60.0

TABLE VI-A (Continued)

Compound	:Sample:c :in mgs:C		:Theoretical Num- : ber for Complete
Formic Acid Acetic Acid N Butyric Acid N Valeric Acid	12.1 10.5 9.6 9.4	0.0 0.0 0.0 0.0	2.0 8.0 20.0 26.0
Maleic Acid Crotonic Acid	6.7 6.8	0.0	12.0 18.0
Glycollic Acid Calcium lactate Tartaric Acid	5.0 5.3 5.0	0.0 0.0 0.0	6.0 12.0 10.0
Mucic Acid Mandelic Acid Benzilic Acid	6.5 5.0 6.3	0.0 0.0 0.0	26.0 34.0 62.0
dl Serine dl Alanine Valine L. Proline	:5.0 app :5.0 app :5.0 app	0.0 0.0 010 0.0 0.0	6.0 10.0 12.0 24.0 18.0
L. Histidine di- hydrochloride	:5.0 app	0.0	16.0
Arginnine Hydro- chloride Cystine Tryrosine Tryptophane dl Lysine Hydro-	5.0 app 5.0 app 5.0 app 5.0 app	39.0 +	18.0 30.0 38.0 46.0
chloride	: :	0.0	: 24.0
dl 1,2,dihydroxy iso-Butyric Acid	1.0	0.0	17.0
dl Erythronic Lactone	1.3	0.0	14.0
dl 1,2,dihydroxy Butyric Acid	1.0	0.0	: 17.0
And the second			

TABLE VI-A (Continued)

Compound	Sample in mgs		Theoretical Num- ber for Complete Oxidation
dl 2,3 dihydroxy: Butyric lactone: dl 1,3 dihydroxy:	7.1	0.0	17.0
Butyric lactone		0.0	17.0
Glucose Mannose Galactose	5.7 4.8 4.0	0.0 0.0 0.0	24.0 24.0 24.0
d-Methyl Glucoside	7.6	0.0	35.0
Penta Acetyl d-Glucose d-Clucosamine	5.7 5.4	0.0	64.0 24.0
Maltose Lactose Cellobiose Trehalose	5.4 5.7 5.7 5.7	0.0 0.0 1.9 1.4	48.0 24.0 48.0 48.0
Fructose Sorbose Benzoin	5.0 6.2 5.5	5.92 9.3 0.0	24.0 24.0 64.0
â-Arabinose 1-Xylose 1-Rhamnose	6.4 6.3 6.6	4.14 4.75 4.82	20.0 26.0 20.0
Pyrogallol Catechol Salicylic Acid Anisole Phenetole	5.2 5.4 6.3 10.0 8.92	17.68 20.1 17.2 + +	24.0 26.0 28.0 34.0 40.0
2 Chlore 5 hy- droxy toluene		11.71	33.0
4 hydroxy 1,2 di- methyl Benzene		20.8	40.0
Methyl Amine Hydrochloride	4.8	0.0	6.0

TABLE VI-A (Continued)

Compound	:Sampl :in mg	e:of s:Oxi :mil	t'l Numbe ml of N dant per limol of bstance	: The : be	oretical Num- r for Complete xidation
Di-methyl Amine Hydrochloride		:	0.0	-	13.0
Ethyl Amine Hydrochloride Ethylene Diamine	and the second second		0.0		12.0
Dihydrochloride		:	0.0	1	10.0
Phenylhydrozine Diphenylamine Benzidine	:10.9 4.9 6.1	:	18.9		26.0 56.0 52.0

TABLE VI-B

Results Obtained by Comparison of Iodine-Chloroform Extractions in the Colorimeter Reaction Time 12 Hours

Compound	: :Average Reading:Amount of:Expt'l Number: :Wt. of:of Colorimeter : Iodine :of ml of N :Theoretical Num- :Sample:on Comparison :Liberated:Oxidant per : ber for Complete :in mgs:with Standard : in mgs. :millimol of : Oxidation : set at 40 : : Substance :								
Meta Hydroxy Benzoic Acid Fructose Arabinose Sorbose	: 0 7	35.0			:	1 70		28 24 20 24	
Cellobiose	; 5.2	:Unknown = 50 :Standard = 11.0		.254	:	.014	:	4g	
Adonitol	5.3	: :Unknown = 45 :Standard = 9.0		.620		.288		22	
Trehalose	4.9	: :Unknown = 50 :Standard = 9.6		.490		.029		48	

Standard Solution 10 cc = 1.269 mg Iodine.

TABLE VI-C

Oxidation of Fructose Sample by Iodic Acid Mixture Varying Reaction Time

Period of Oxida- tion	And a second sec	:Sampl	e: s: :		:Theoretical Num- : ber for Complete
40 min. 50 min. 1 hr.		7-756-5		6.58 7.60 6.94 7.08	24.0 11 11
1 hr. 15 min.	Û.	: 5.8	:	6.59	Ĥ
1 hr. 30 min.	Î	6.2		7.02	Ĥ

The above results indicate the period of oxidation, in this case at least, could be shortened very easily as the reaction appears to go nearly to completion in a very short time.

TABLE VI-D

Oxidation of Fructose in the Dark and Directly Under a 200 Watt Electric Lamp by Iodic Acid After 30 Minutes

		f:Mi	Îliliters	of	N Oxidan	t:be	neoretical Num- er for Complete Oxidation
		s:	Reaction the Dark	:	Reaction	:	
Fructose:	1		6.38	:	7.66 7.6	:	24.0
	25	÷	2.27	:	7.69	÷	11
	79	:	2.29 2.1	-	6.50 5.80		"

Direct comparison of the values in each case shows a much higher value for the second reaction thereby producing evidence that light is a direct promoter of this reaction.

Potassium Periodate in Dilute Sulphuric Acid.

The use of iodic acid as an oxidizing agent suggested the use of periodic acid, but as previous investigations of this reagent have been quite extensive (5, 8, 9) the amount of work done was limited. Previous workers, however, indicated the reaction was far more free from difficulties than was found to be the case. The incompleteness of the reaction in many instances led to the establishment of a definite temperature of 25° C. in place of the variable room temperatures formerly used. The mechanism of the reaction as formulated by Malaprade (11, 12) in which the carbon-to-carbon bonds in the glycols were broken at each carbon atom thus forming end products of formaldehyde and formic acid, was accepted. He also showed that the oxidation was accomplished by the reduction of periodic acid to iodic acid.

The procedure used by Malaprade (8) was modified slightly by using a 0.1 molar solution of potassium periodate dissolved in 10 per cent sulphuric acid in place of crystalline periodic acid or potassium di-meso periodate dissolved in excess of the same solvent. This slight modification of the original reagent was standardized without difficulty upon mannitol solutions. The results were compared to the original values given (8) before it was used.

The samples were introduced into clean 25 ml erlenmeyer flasks together with a mixture of 1 ml of potassium periodate in 10 per cent sulphuric acid plus 2 ml of water. The flasks were stoppered and allowed to set for twenty hours at 25° C. At the end of this time they were removed, the contents rinsed into 250 ml erlenmeyer flasks, diluted to 100 ml, and 10 ml of 10 per cent sulphuric acid added. Sodium bicarbonate (0.75 gram) was added to produce an atmosphere of carbon dioxide plus 1.5 grams of potassium iodide. The amount of oxidizing agent reduced to iodic

acid was determined by the difference in the thiosulphate-starch indicator titration before and after the reaction had taken place.

TABLE VII

Results Obtained Using Periodic Acid Mixtures in Dilute Sulphuric Acid

Compound	Sample in mgs	Expt'l Number of ml of N Oxidant per millimol of Substance	: Theoretical ; ber for	Num-	
Mannitol Mannitol	87.325 1.0	10.2 9.45	10.0		
2,3 d hydroxy Butyric Lactone			2.0		
1,2 hydroxy Butyric Acid 1,3 hydroxy	0.973	1.0	2.0		
Butyric Lactone	0.90	0.0	0.0		
	1.004	5.85	4.0		
isobutyric Acid	1.016	2.08	2.0		
Malic Acid			: 0.0		
Lactic Acid Tartaric Acid			0.0 2.0		

Conclusions

1. Seven oxidizing solutions were used in the study of the partial oxidation of organic compounds. The extent of oxidation of different compounds was determined by titration of the unused amount of reagent. The number of equivalents of oxygen consumed per mol in relation to the number of equivalents necessary for complete oxidation was used as a basis of comparison. From the data thus obtained the end products were postulated and the specificity as to organic groups, if any, noted.

2. The results obtained by use of potassium permanganate, potassium dichromate, and ceric sulphate solutions under the various conditions tried showed they were not specific, but exhibited tendency to oxidize the compounds completely.

3. In the case of iodic acid a marked selectivity was noticed. Certain types of compounds such as aliphatic alcohols, with the exception of methanol, aldehydes and ketones, were oxidized. Aldohexoses and most polyhydric alcohols were unattacked. The extent of the selectivity is better obtained by examination of table VI.

4. Former work (8, 9) using periodic acid solutions under oxidizing conditions was extended to include the hydroxy butyric acids.

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