The Institute of Paper Chemistry
Appleton, Wisconsin

Doctor's Dissertation

The Oxidation of Simple Organic Compounds
With Aqueous Chlorine Dioxide Solutions

Roger A. Somsen

June, 1958
THE OXIDATION OF SIMPLE ORGANIC COMPOUNDS
WITH AQUEOUS CHLORINE DIOXIDE SOLUTIONS

A thesis submitted by

Roger A. Somsen
B. S. 1953, University of Wisconsin
M. S. 1955, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1958
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PRESENTATION OF PROBLEM</td>
<td>3</td>
</tr>
<tr>
<td>EXPERIMENTAL PROCEDURES</td>
<td>6</td>
</tr>
<tr>
<td>Organic Compounds Used</td>
<td>6</td>
</tr>
<tr>
<td>Chlorine Dioxide Generation and Purification</td>
<td>7</td>
</tr>
<tr>
<td>Preparation of Reaction Mixtures</td>
<td>7</td>
</tr>
<tr>
<td>Determination of Chlorine Dioxide Reaction Rates</td>
<td>9</td>
</tr>
<tr>
<td>Determination of Organic Reaction Products</td>
<td>10</td>
</tr>
<tr>
<td>Nongaseous Reaction Products</td>
<td>10</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>17</td>
</tr>
<tr>
<td>EXPERIMENTAL RESULTS</td>
<td>19</td>
</tr>
<tr>
<td>Kinetic Studies at pH 7</td>
<td>19</td>
</tr>
<tr>
<td>Kinetic Studies at pH 1</td>
<td>25</td>
</tr>
<tr>
<td>Organic Reaction Products</td>
<td>31</td>
</tr>
<tr>
<td>Discussion and Summary</td>
<td>35</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>41</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>43</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>45</td>
</tr>
<tr>
<td>I. Preparation and Analysis of Aqueous Chlorine Dioxide Solutions</td>
<td>45</td>
</tr>
<tr>
<td>II. Quantitative Transfer of Chlorine Dioxide Solutions</td>
<td>48</td>
</tr>
<tr>
<td>III. Gas Chromatography Apparatus</td>
<td>51</td>
</tr>
<tr>
<td>Physical Components</td>
<td>51</td>
</tr>
<tr>
<td>Detection Components</td>
<td>55</td>
</tr>
<tr>
<td>Column Preparation</td>
<td>56</td>
</tr>
<tr>
<td>Operation</td>
<td>59</td>
</tr>
<tr>
<td>IV. Kinetic Data at pH 7</td>
<td>63</td>
</tr>
<tr>
<td>V. Kinetic Data at pH 1</td>
<td>68</td>
</tr>
<tr>
<td>VI. Calculation Methods for Kinetics Constants at pH 1</td>
<td>75</td>
</tr>
</tbody>
</table>
INTRODUCTION

It was originally thought that chlorine dioxide was specific in its bleaching reactions, attacking only the noncarbohydrate material present in the cellulose. This concept was based upon the work of Schmidt and Graumann (1) who reported that cellulose, oxidized cellulose, sugars, and other similar compounds were not attacked appreciably during treatments with chlorine dioxide at room temperature for twenty-four hours. Staudinger and co-workers (2, 3), however, found that the degree of polymerization (D.P.) of cellulose was lowered by treatment with chlorine dioxide, while Jeanes and Isbell (4) showed that aldose sugars were attacked slowly.

Marked modification of cellulose was reported by Lapèze and Dardelet (5) with the application of 40% chlorine dioxide based on the cellulose at 70°C. Their results, under these relatively drastic experimental conditions, showed that marked decreases in D.P. and alpha-cellulose content and increases in copper number and carboxyl content occurred over the pH range 2 to 7. When conventional amounts of applied chlorine dioxide were used on normally bleached sulfate and sulfite pulps, however, no appreciable change in either D.P. or hot alkali solubility were noted (6-9). On the other hand, the carboxyl content of a strongly overbleached pulp (treated with an acid chlorine bleach liquor to produce carbonyl groups) increased greatly upon treatment with chlorine dioxide, while the carbonyl content decreased. Therefore, it is apparent that while the hydroxyl groups in cellulose are quite resistant to attack by chlorine dioxide, any carbonyl groups resulting from overbleaching are quite susceptible to attack.
Ethanol is the only simple compound containing a functional grouping present in cellulose whose reaction with chlorine dioxide has been studied (2). Upon adding a solution of potassium chlorate dropwise to a mixture of equal volumes of ethanol and sulfuric acid, ethyl acetate, chloroform, chlorohydrin, chloral, and chloroacetic acid were identified as reaction products. Since the reaction conditions in this ethanol oxidation are far more severe than would be the case with an oxidation in dilute aqueous solution, the reaction products of the oxidations may be quite different.
PRESENTATION OF PROBLEM

Although the importance of chlorine dioxide as a bleaching agent increases each year, little is known about its reactions with carbohydrates and other types of molecules. In order that the most intelligent use can be made of its bleaching properties, it is desirable that a complete understanding of its chemical reactions be obtained.

A thorough study of the reactions of chlorine dioxide with cellulose is difficult because this reaction system is heterogeneous, the analytical methods for the functional groups present in an oxidized cellulose are not good, and the methods of hydrolyzing an oxidized cellulose to small identifiable compounds are open to question. These problems can be eliminated by a study of simple molecules containing only one of the several functional groupings which have been proposed for cellulose at various degrees of oxidation (10)—α-glycol, α-hydroxyketone, and α-diketone for the C₂ and C₃ positions in the anhydroglucose ring and primary alcohol and aldehyde for the C₆ position. Such a study would also provide a foundation for further studies with more complex molecules, such as sugars and cellulose.

The compounds chosen for study were simple molecules containing these proposed functional groupings. These compounds are identified and compared with the structures of hypothetical oxidized celluloses in Figure 1. n-Butyraldehyde was chosen for study at higher temperatures because of the low boiling point of acetaldehyde. The rates of reaction between chlorine dioxide and each of these compounds in dilute aqueous solution were to be determined as a function of temperature at pH 1 and 7. The oxidizing
properties of chlorine dioxide were to be characterized by the determination of the organic reaction products from the oxidations of diacetyl and 2,3-butaneediol at pH 1.
Figure 1. Comparison of Structures of Hypothetical Oxidized Celluloses and Analogous Simple Compounds
EXPERIMENTAL PROCEDURES

ORGANIC COMPOUNDS USED

The source and method of purification for each of the starting organic compounds are listed below:

1. The 2,3-butanediol (EK P3400) was purified by the method of Leslie and Castagne (11). The fraction boiling at 179-180°C was collected.

2. Acetoin (EK P3788) was purified by the method of Westerfeld (12). The fraction boiling at 141-142°C was collected and stored under refrigeration.

3. Diacetyl (EK 1591) was purified by the method of Westerfeld (12). The fraction boiling at 89-90°C was collected and stored under refrigeration.

4. Acetaldehyde (EK 468) was purified by fractional distillation under nitrogen.

5. The n-butyraldehyde (EK 440) was purified by drying three times over Drierite and fractionally distilling under nitrogen through a Vigreux column. The fraction boiling at 74°C was collected and transferred to 4-ml screwcap vials in a nitrogen atmosphere. These vials were stored under refrigeration and one vial was opened for each sample required.

6. The ethanol was Rossville Gold Shield Alcohol, 200 proof, obtained from Commercial Solvents Corporation. It was purified by the method of McComb and McCready (13).
Aqueous solutions of purified chlorine dioxide were prepared by passing a chlorine-air mixture through two sodium chlorite columns arranged in series. The unreacted chlorine was removed by passing the chlorine-chlorine dioxide-air mixture through a saturated aqueous solution of barium hydroxide. The chlorine dioxide was then dissolved in triple distilled water containing enough nitric acid to make the pH about 1. The presence of acid prevents hydrolytic disproportionation of chlorine dioxide. The concentrations of chlorine dioxide and chlorine were determined by titration of a neutral sample and an acid sample with N/10 sodium thiosulfate. No chlorine was found when the generator was operating properly. The details of this procedure are given in Appendix I.

PREPARATION OF REACTION MIXTURES

Reaction mixtures were prepared from three solutions. The details of the preparation of each of these solutions are listed below:

1. Buffer Solution. For reactions at pH 1, 25 ml. of nitric acid-potassium nitrate buffer (105 g. potassium nitrate and 51 ml. of nitric acid added to 978 ml. triple distilled water) was added for each 100 ml. of total reaction mixture. For reactions at pH 7, 45 ml. of mono-dipotassium phosphate buffer (400 g. dipotassium phosphate and 50 ml. 85% phosphoric acid added to 1800 ml. of triple distilled water) was added for each 100 ml. of total reaction mixture. Buffer catalysis effects, if present, were shown by adding only 80% of the above amount of buffer at pH 1 and 67%
at pH 7. When buffer concentration was found to affect reaction rate, 40 ml. of 0.775 molal sodium sulfate solution was added to a low buffer concentration mixture to give the finished reaction mixture the same ionic strength as a regular buffer concentration reaction mixture. In this manner, ionic strength effects upon reaction rate were separated from buffer catalysis effects.

2. **Organic Solution.** The starting organic compound was weighed into a volumetric flask and diluted to volume with triple distilled water. The volume of this solution necessary to give the required reaction mixture concentration (generally 0.010M) was pipetted into the buffer solution.

3. **Chlorine Dioxide Solution.** Sufficient purified and thermostated chlorine dioxide solution was added to the mixture with the transfer device described in Appendix II to make the reaction mixture about 0.0100M in chlorine dioxide. This device minimized transfer loss of chlorine dioxide because the air space above the solution was kept saturated with chlorine dioxide.

The buffer solution was added to a volumetric flask at least four hours before the oxidation was begun so that its temperature could equilibrate with that of the bath in which the reaction was to be run. The organic solution was added just before the chlorine dioxide solution and the total was then diluted to volume with triple distilled water at the oxidation temperature. Time zero was determined when the chlorine dioxide solution was added. After thorough mixing, the reaction mixture was ready for either chlorine dioxide rate studies or organic reaction product analysis.
For studies of the effect of surface area upon reaction rate, 0.2 g. of glass fibers was dispersed in the reaction mixture. These fibers had a weighted average fiber diameter of 1.64μ and a surface area of 10,840 cm.²/g.

DETERMINATION OF CHLORINE DIOXIDE REACTION RATES

Due to the volatility of chlorine dioxide, rate studies required that the reaction be carried out in a vessel with a variable volume so that there was no gas phase above the reaction mixture. Hypodermic syringes proved effective for this use. Light effects were minimized by covering the syringes with aluminum foil. The completed reaction mixture was transferred to the syringe by the application of air pressure to the surface of the reaction mixture (see Figure 2A). When the syringe was filled, the stopcock was closed, the delivery tube attached, and the unit (see Figure 2B) placed in a constant temperature bath. Samples for the determination of chlorine dioxide concentration were removed from the delivery tube.

The following method of iodometric analysis was used for the determination of total active chlorine concentration in the reaction mixture samples.

Ten milliliters of buffer solution (100 g. of dipotassium phosphate dissolved in 450 ml. of distilled water and adjusted to a pH of 7.0-7.5 with phosphoric acid), 10 ml. of 4N sulfuric acid, and 0.5 g. potassium iodide were mixed in a 125-ml. Erlenmeyer flask. A portion of this mixture was added to a 10-ml. volumetric flask which was then weighed. The reaction mixture sample (about 1 ml.) was then added to this flask and the flask
weighed again. The contents of the volumetric flask were added quantitatively to the Erlenmeyer flask, mixed, and allowed to stand for two minutes. The sample was then titrated with N/100 sodium thiosulfate using Thyodene indicator near the end point. The sample weight was converted to volume by determining the density of the reaction mixture at 25°C.

The concentration of total active chlorine in the reaction mixture was calculated from the following equation:

\[
\text{conc. total active Cl}, \text{ meq./l.} = 10 \frac{V}{d \cdot w}
\]

where \( V \) was the volume of N/100 sodium thiosulfate solution, \( d \) was the reaction mixture density, and \( w \) was the sample weight.

DETERMINATION OF ORGANIC REACTION PRODUCTS

NONGASEOUS REACTION PRODUCTS

The scheme for the separation of the completed reaction mixture resulting from the oxidation of diacetyl and 2,3-butanediol at pH 1 into fractions for further analyses is given in Table I. Because gas chromatography columns are not capable of handling large quantities of water, it was necessary to extract the solution with an organic solvent. This extraction with redistilled Freon-TF solvent was carried out in a continuous Schmall liquid-liquid extractor (14) for denser liquids. Each 100 ml. of reaction mixture was extracted with 200 ml. of redistilled Freon-TF. It was necessary to concentrate this extract because of the small amount of organic material dissolved in the Freon-TF solvent. The concentration was accomplished using
Figure 2A
Reaction Mixture Transfer

Figure 2B
Complete Hypodermic Syringe Reaction Vessel

Figure 2. Equipment for Determining Chlorine Dioxide Consumption
a stainless steel wire-wound fractionating column suggested by Dr. E. F.
Thode, which was operated at a reflux ratio of about 4:1 with the distillation
pot immersed in a water bath at 58°C. The extraction was concentrated
to a final volume of about 25 ml. for further analysis.

The volatile fatty acids present in the extracted reaction mixture were
removed by steam distillation (200 ml. of distillate was collected for each
100 ml. of reaction mixture distilled). The concentrated distillate was
purified by the addition of ethanol to precipitate inorganic salts.

Only three fractions—concentrated Freon-TF extract, steam distillation
residue, and steam-distilled extracted reaction mixture—were analyzed for
organic components. A gas chromatography apparatus (see Appendix III for
details) was constructed to determine the volatile material present in the
concentrated Freon-TF extractions. The experimental conditions under which
these analyses were performed are listed in Table II. The components of the
mixture were removed from the gas stream by freezing them out into separate
glass U-tubes. A suitable solvent was added to each U-tube and the infra-
red spectrum was obtained by running this solution against the solvent on
a Perkin-Elmer Model 21 Recording Spectrophotometer. The compound was
identified by comparison with known spectra. The amount of material in
each gas chromatographic fraction was determined from standard Beer’s Law
curves. The curves for diacetyl and 2,3-butanediol are given in Figures 3
and 4, respectively.

Because the absorption spectrum of the carbonyl material from the 2,3-
butanediol oxidation was not sufficiently strong for identification, the
2,4-dinitrophenylhydrazine derivative was prepared (15).
TABLE I

SEPARATION OF ORGANIC REACTION PRODUCTS

| Reaction Mixture | Neat to 0°C | Quenched Reaction Mixture | KI + Na₂S₂O₃ | Neutralized Reaction Mixture | Na₂SO₄ | Saturated Reaction Mixture | Freon-TF |

**Freon-TF Extract**

| Concentrated Freon-TF Extract | Distillate | Extracted Reaction Mixture | Steam Distill |

**Steam Distillate**

| KOH | Alkaline Solution (pH 9) | Concentrate |

**Concentrated Solution**

| Water | EtOH |

**Purified Solution**

| Inorganic Salts | Concentrate |

**Concentrated Solution**

| Water-EtOH | EtOH |

**Purified Solution**

| Inorganic Salts | Evaporate to Dryness |

Steam Distillation Residue

1 Fractions analyzed
TABLE II

OPERATING CONDITIONS OF GAS CHROMATOGRAPHY APPARATUS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column support material</td>
<td>C-22 crushed firebrick</td>
</tr>
<tr>
<td>Column liquid</td>
<td>DC Silicone 710 Fluid</td>
</tr>
<tr>
<td>Liquid content on support material</td>
<td>29% (w/w)</td>
</tr>
<tr>
<td>Column diameter</td>
<td>1/2 in.</td>
</tr>
<tr>
<td>Column length</td>
<td>12 2/3 ft.</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>70, 100°C.</td>
</tr>
<tr>
<td>Helium flow rate</td>
<td>200 ml. (S.T.P.)/min.</td>
</tr>
<tr>
<td>Chart speed</td>
<td>12 in./min.</td>
</tr>
<tr>
<td>Amplifier volume</td>
<td>maximum</td>
</tr>
<tr>
<td>Bridge voltage</td>
<td>6.0 v.</td>
</tr>
</tbody>
</table>

All three of the fractions were analyzed for nonvolatile material by paper chromatography. Ethanol:ammonia (100:1) solvent was used to develop acidic material. The presence of acids was shown by spraying the sheets with formaldehyde (4% solution in ethanol) to destroy the ammonium salts, drying the sheets, and then spraying the dried sheets with a methyl orange (1 g./l. in water) solution. Ethyl acetate:acetic acid:formic acid:water (18:3:1:4) solvent was used to develop carbonyl material. The presence of carbonyl material was shown by spraying the sheets first with a 2,4-dinitrophenylhydrazine (0.5 g. in 250 ml. 3N hydrochloric acid) solution and then with a 10% solution of potassium hydroxide in water. The component(s) of the steam distillation residue was also identified by the infrared spectrum of a potassium bromide pellet. The quantity of this residue was determined by its weight.
Figure 3. Beer's Law Curve for Diacetyl at 8.9μ
Figure 4. Beer's Law Curve for 2,3-Butanediol at 11.33 μ
CARBON DIOXIDE

The carbon dioxide evolved during the oxidations of diacetyl and 2,3-butanediol was determined with the equipment outlined in Figure 5. When the oxidation was completed, the Day pinchclamps were removed and nitrogen was bubbled through both a blank reaction mixture (contained no organic material) and an organic reaction mixture. Excess chlorine dioxide was removed by washing the gas stream with acidic potassium iodide, and carbonyl material was absorbed in the 2,4-dinitrophenylhydrazine solution. After drying the gas stream with Drierite and magnesium perchlorate, the carbon dioxide was absorbed quantitatively on Ascarite. The difference in weight increase between the blank and organic oxidation was a direct measure of the carbon dioxide evolved by the oxidation mixture.
Figure 5. Apparatus to Determine Carbon Dioxide Evolution
EXPERIMENTAL RESULTS

KINETIC STUDIES AT pH 7

The experimental data upon which the following observations are based are listed in Appendix IV. Figures and tables are given below to illustrate these observations.

The effect of temperature upon the rate of decomposition of blank chlorine dioxide solutions buffered at pH 7 is shown in Figure 6. It is apparent that these solutions are quite unstable at this pH value. Two reactions have been proposed to account for the decomposition of neutral and acid chlorine dioxide solutions:

\[
\text{ClO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ClO}_2^- + \text{ClO}_3^- + 2\text{H}^+ \quad (16), \quad \text{and}
\]

\[
6\text{ClO}_2 + 3\text{H}_2\text{O} \rightarrow 5\text{HClO}_3 + \text{HCl} \quad (17).
\]

It was reported that in unbuffered solutions the rate of decomposition was slow in both acid and neutral systems. This is definitely not the case, however, in solutions buffered at pH 7 with phosphate.

A typical reaction plot at pH 7 is illustrated in Figure 7. The amount of chlorine dioxide consumed in the oxidation of diacetyl appears to be appreciable, but consumption values must be known numerically for a reaction kinetics study. The difference between the blank and organic oxidation analyses may be assumed to be a direct measure of the oxidant consumption. The organic oxidation, however, results in a faster buildup of inorganic reaction products as well as a lower chlorine dioxide concentration than
that in the blank. Both of these effects result in a lower rate of chlorine dioxide decomposition in the oxidation mixture. As a result, the blank solution overcompensates and conclusions based on this difference technique are not theoretically sound.

Since chlorate ion is formed in both of the proposed decomposition equations, and since no chlorate ion should be produced during the oxidations of organic compounds, the chlorate ion concentration in a reaction mixture should be a direct measure of the amount of decomposed chlorine dioxide. Techniques for the determination of chlorate, however, were found to be both insensitive and lengthy and, therefore, not suitable for use in a kinetics study. Consequently, the difference technique was applied to several oxidations and several interesting curves were obtained (see Figure 8). The reaction rate would appear to be zero order over an extended period of the reaction when the rate of consumption of active chlorine is not too rapid and when the difference between the oxidant concentration in the blank and organic oxidation is not too great. When these two conditions are not fulfilled, plots similar to Curve B (Figure 8) are obtained. It should be noted, however, that neither of the apparent zero order plots (Curves A and C, Figure 8) could be extrapolated to zero consumption at zero time. This effect might be the result of an initial, very rapid reaction which is followed by a second, slower reaction. It is this possible second reaction that would be illustrated in Figure 8.

The stability of the starting compounds toward chlorine dioxide attack at pH 7 is expressed in Table III in terms of the maximum temperature at
Figure 6. Effect of Temperature Upon Rate of Decomposition of Chlorine Dioxide Solutions Buffered at pH 7 with Phosphate
Figure 7. Reaction Curve for Diacetyl at pH 7 and 10°C.
which no reaction was detectable. Hydroxyl compounds are apparently very
stable to chlorine dioxide attack at pH 7 even at 80°C. This stability
decreases rapidly, however, upon the substitution of carbonyl groups for
hydroxyl groups. To illustrate, both diacetyl and acetaldehyde react
rapidly at 10°C.

TABLE III

STARTING COMPOUND STABILITY TO CHLORINE DIOXIDE AT pH 7

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>&gt;80</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>&gt;80</td>
</tr>
<tr>
<td>Acetoin</td>
<td>10</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

a Maximum temperature at which no reaction was noted.

The effect of buffer concentration upon the rate of oxidant consump-
tion at pH 7 is shown in Figure 9. An increase in reaction rate with
increased buffer concentration could be produced either by buffer catalysis
or by change in ionic strength. Buffer catalysis provided the only expla-
nation for this effect, however, when it was found that the addition of
sodium sulfate to the low buffer concentration reaction mixture did not
change the reaction rate. Such buffer catalysis phenomena have been obser-
vied in many halogen oxidation systems (18, 19) and were shown to be caused
by changes in the concentration of the acid form of the buffer.
Figure 8. Total Active Chlorine Consumed at pH 7 as Determined by the Difference Technique.
In summary, the experimental kinetics observations at pH 7 are qualitative in nature rather than quantitative because of the decomposition of the chlorine dioxide solutions and of the presence of buffer catalysis. It was shown, however, that the hydroxyl compounds are much more resistant to attack by chlorine dioxide than compounds containing carbonyl groups. The reactions with acetoin and acetaldehyde did appear, however, to be of zero order.

KINETIC STUDIES AT pH 1

The experimental data upon which the following observations are based are listed in Appendix V. Figures and tables are given below to illustrate these observations.

The stability of the various functional groupings toward chlorine dioxide attack at 80°C. is illustrated in Figure 10. These groupings can, therefore, be ranked in the following order of stability: primary alcohol > α-glycol > α-hydroxyketone > α-diketone > aldehyde. This is basically the same order that was noted at pH 7 (see Table III).

The curve for n-butyraldehyde at 80°C. appears to be quite different, however, from that of the other compounds. When the reaction is carried out at 50°C. (see Figure 11), however, the reaction rate plot shows that the total reaction is the sum of two successive apparent zero order reactions. The first reaction of this sequence is much more rapid than the second.

It is possible to analyze the kinetics of these oxidations directly from the experimental data because blank chlorine dioxide solutions buffered
Figure 9. Effect of Phosphate Buffer (pH 7) Concentration upon Rate of Reaction with Diacetyl at 10°C.
at pH 1 were found to be stable. Each oxidation followed an apparent zero order reaction rate. The rate constants listed in Table IV for these reactions were calculated from rate plot slopes. The activation energies and temperature coefficients listed in Table V are based upon these rate constants (see Appendix VI for calculation methods). The activation energies listed are of the magnitude expected for reactions occurring under these experimental conditions since values of about 20 kg.-cal./mole are normal for reactions at ordinary temperatures (35, p. 1091). The initial reaction in the n-butyraldehyde oxidations shows a markedly lower activation energy. This result, however, would be expected from the greater reactivity of the aldehyde group over that of the ketone and hydroxyl groups under the same experimental conditions.

In contrast to the buffer catalysis phenomenon noted at pH 7, buffer concentration was found to have no effect on reaction rate at pH 1. Since surface area often affects the rate of zero order reactions, its effect at pH 1 was studied in the oxidation of acetoin at 60 and 80°C. When the free surface area in the reaction syringe was doubled by the addition of finely chopped glass fibers, there was no apparent change in reaction rate. Since acetoin was thought to be typical of the type of compounds being studied, no surface effects would be expected with the other compounds.

In summary, the oxidations at pH 1 were found to follow apparent zero order reaction rates and were not affected by either buffer concentration or surface area. Hydroxyl groups were again found to be more stable to chlorine dioxide attack than carbonyl groups.
Figure 11. Kinetics Curves for n-Butyraldehyde at pH 1
### TABLE IV

REACTION RATE CONSTANTS AT pH 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature, °C</th>
<th>$k_a \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>80</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.65</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>80.5</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>2.6</td>
</tr>
<tr>
<td>Acetoin</td>
<td>80.5</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.9</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>80.5</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>9.8</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>80b</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>60b</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>50c</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>40c</td>
<td>4.3</td>
</tr>
</tbody>
</table>

*a (Equivalents total active chlorine)/(liter)(minute).

b Based on final rate, Figure 11.

c Based on initial rate, Figure 11.

### TABLE V

ACTIVATION ENERGIES AND TEMPERATURE COEFFICIENTS AT pH 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature, °C</th>
<th>$E_a^a$</th>
<th>Temperature Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>70, 80</td>
<td>21</td>
<td>2.5</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>70, 80</td>
<td>19</td>
<td>2.2</td>
</tr>
<tr>
<td>Acetoin</td>
<td>60, 80</td>
<td>18</td>
<td>2.1</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>60, 80</td>
<td>21</td>
<td>2.9</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>40, 50b</td>
<td>6.8</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>60, 80c</td>
<td>14</td>
<td>1.7</td>
</tr>
</tbody>
</table>

*a Kilogram-calories/mole.

b Based on initial rate.

c Based on final rate.
The results from the chromatographic analyses of the three fractions from the oxidations of diacetyl and 2,3-butanediol at pH 1 are listed in Table VI and Table VII, respectively. Acetic acid, isolated as potassium acetate, is the only nongaseous reaction product that was found in large enough quantities to be identified by infrared spectra and paper chromatography in each oxidation. The formation of acetic acid indicates that these functional groupings are oxidized with a cleavage of carbon-carbon bonds. This cleavage results in the formation of acetic acid from both α-diketone and α-glycol groupings.

Gas chromatographic analysis of the concentrated Freon-TF extraction from the oxidation of 2,3-butanediol showed the presence of a very small amount of material of low retention volume, approximately that for diacetyl. The low retention volume indicates that the material had a low boiling point (below 100°C.) and the shape of the peak (blip), which appears on the recorder, shows that it probably did not contain either hydroxyl or carboxyl groups. Infrared spectrum analysis was difficult because the extremely small amount of material present produced only small absorption peaks. The spectrum, however, did show the three major absorption bands of diacetyl (5.81, 7.38, and 8.99µ). The carbonyl band at 5.81µ, however, appears as a shoulder on a stronger band at 5.77µ. Absorption at this wavelength may be attributed to α-halogen substituted ketones, α-halogen substituted acids, or saturated aliphatic aldehydes. The remaining bands in the spectrum were not of sufficient strength to allow correlations of spectra with structure. The 2,4-dinitrophenylhydrazine derivative(s) of this material was prepared and,
TABLE VI

REACTION PRODUCT ANALYSIS FOR DIACETYL OXIDATION

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Experimental Results</th>
<th>Gas Chromatography</th>
<th>Paper Chromatography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrated Freon-TF extract</td>
<td>Unreacted diacetyl</td>
<td>No acid spots</td>
<td>No carbonyl spots</td>
</tr>
<tr>
<td></td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam distillation residue</td>
<td>- -</td>
<td>KOAc\textsuperscript{b} present</td>
<td>No carbonyl spots</td>
</tr>
<tr>
<td>Steam distilled extracted reaction mixture</td>
<td>- -</td>
<td>No acid spots</td>
<td>No carbonyl spots</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Oxidation carried out at pH 1 and 60°C for 8 hr.

\textsuperscript{b} Potassium acetate

TABLE VII

REACTION PRODUCT ANALYSIS FOR 2,3-BUTANEDIOL OXIDATION

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Experimental Results</th>
<th>Gas Chromatography</th>
<th>Paper Chromatography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrated Freon-TF extract</td>
<td>Very small amount</td>
<td>No acid spots</td>
<td>No carbonyl spots</td>
</tr>
<tr>
<td></td>
<td>carbonyl material</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>present</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam distillation residue</td>
<td>- -</td>
<td>KOAc\textsuperscript{b} present</td>
<td>No carbonyl spots</td>
</tr>
<tr>
<td>Steam distilled extracted reaction mixture</td>
<td>- -</td>
<td>No acid spots</td>
<td>No carbonyl spots</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Oxidation carried out at pH 1 and 80°C for 19 hr.

\textsuperscript{b} Potassium acetate
without purification, was found to char at 288-292°C. Diacetyl bis(2,4-dinitrophenylhydrazone) chars at 315°C. Although no irrevocable proof for the presence of diacetyl has been established, both the infrared spectrum of the gas chromatographic fraction and decomposition point of the derivative indicate that it may be present in this trace material.

The possible presence of diacetyl in this oxidation mixture indicates that the mechanism of the 2,3-butanediol oxidation involves the conversion of at least part of the α-glycol groupings to α-diketone groupings before the molecules were split into carboxylic acid molecules. The concentration of diacetyl could never become very large, however, because of its rapid oxidation by chlorine dioxide to acetic acid and carbon dioxide.

The material balance summaries for the oxidations of diacetyl and 2,3-butanediol at pH 1 are presented in Table VIII and Table IX, respectively. These data show that carbon dioxide as well as acetic acid have been isolated as reaction products. The two successive apparent zero order reactions noted for the oxidations of n-butyraldehyde (see Figure 11) can be explained on the basis of the formation of a carboxylic acid and carbon dioxide. The initial rapid reaction could be the oxidation of n-butyraldehyde to n-butyric acid while the second slower reaction could be the degradation of n-butyric acid to carbon dioxide.

The following three points should be noted in considering the quantitative data presented in Table VIII and Table IX:

1. There was undoubtedly some loss of diacetyl during the concentration of the Freon-TF extract during Run 68, and no unreacted 2,3-butanediol
TABLE VIII

MATERIAL BALANCE SUMMARY FOR OXIDATION OF DIACETYLE\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run no.</th>
<th>68</th>
<th>71</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO\textsubscript{2}</td>
<td>0.0103M</td>
<td>0.0139M</td>
</tr>
<tr>
<td>Diacetyl</td>
<td>0.0100M</td>
<td>0.0100M</td>
</tr>
<tr>
<td>Total volume, ml.</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Reaction time, hr.</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>ClO\textsubscript{2} consumed, mmol.</td>
<td>9.6</td>
<td>-</td>
</tr>
<tr>
<td>Compounds determined, mmol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6.3</td>
<td>-</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>Unreacted diacetyl</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Compound yields\textsuperscript{b}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>32</td>
<td>-</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Unreacted diacetyl</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Total yield, %</td>
<td>48\textsuperscript{c}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Oxidations carried out at pH 1 and 60°C.
\textsuperscript{b} Molar percentage of initial diacetyl.
\textsuperscript{c} Total yield could not be determined from any single run (p.11).

TABLE IX

MATERIAL BALANCE SUMMARY FOR OXIDATION OF 2,3-BUTANEDIOL\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run no.</th>
<th>69</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO\textsubscript{2}</td>
<td>0.0119M</td>
<td>0.0121M</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>0.0101M</td>
<td>0.0103M</td>
</tr>
<tr>
<td>Total volume, ml.</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Reaction time, hr.</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>ClO\textsubscript{2} consumed, mmol.</td>
<td>10.3</td>
<td>-</td>
</tr>
<tr>
<td>Compounds determined, mmol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4.5</td>
<td>-</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Unreacted 2,3-butanediol</td>
<td>- \textsuperscript{b}</td>
<td>-</td>
</tr>
<tr>
<td>Compound yields\textsuperscript{c}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Unreacted 2,3-butanediol</td>
<td>- \textsuperscript{b}</td>
<td>-</td>
</tr>
<tr>
<td>Total yield, %</td>
<td>24\textsuperscript{d}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Oxidations carried out at pH 1 and 80°C.
\textsuperscript{b} None found but test sensitivity low.
\textsuperscript{c} Molar percentage of initial 2,3-butanediol.
\textsuperscript{d} Total yield could not be determined from any single run (page 11).
was recovered during Run 69. Consequently, the total yield values reported would be low.

2. While the technique for determining carbon dioxide was quantitative, only 74% of the acetic acid present in a solution of known concentration could be recovered in the steam distillation residue. Therefore, the values for recovered acetic acid would probably be low.

3. The yields of acetic acid and carbon dioxide could not be reported for the same reaction mixture. As a result, there is some question as to whether or not the same degree of oxidation was accomplished for each of the determinations.

Bearing these points in mind, Table X was constructed upon the assumption that the oxidations followed the equations below:

\[
5 \text{CH}_3\text{COCOCH}_3 + 2 \text{ClO}_2 + 6 \text{H}_2\text{O} \rightarrow 10 \text{CH}_3\text{COOH} + 2 \text{HCl}
\]

\[
5 \text{CH}_3\text{COCOCH}_3 + 18 \text{ClO}_2 \rightarrow 20 \text{CO}_2 + 6 \text{H}_2\text{O} + 18 \text{HCl}
\]

\[
5 \text{CH}_3\text{CHOHCHOHCH}_3 + 6 \text{ClO}_2 \rightarrow 10 \text{CH}_3\text{COOH} + 6 \text{HCl} + 2 \text{H}_2\text{O}
\]

\[
5 \text{CH}_3\text{CHOHCHOHCH}_3 + 22 \text{ClO}_2 \rightarrow 20 \text{CO}_2 + 14 \text{H}_2\text{O} + 22 \text{HCl}
\]

It is immediately apparent that in no instance has more than 50% of the consumed chlorine dioxide or unrecovered organic starting material been determined. If chlorine dioxide in acid solution is reduced to chloride ion (17), the assumed equation should be correct and, therefore, the low consumption and recovery values must be the result of incomplete recovery of acetic acid and carbon dioxide and/or formation of other reaction products which were not detected.

**DISCUSSION AND SUMMARY**

Reactions exhibiting zero order mechanisms are not commonplace.
## TABLE X

### EFFICIENCY OF EXPERIMENTAL METHODS

<table>
<thead>
<tr>
<th></th>
<th>Diacetyl Oxidation</th>
<th>2,3-Butanediol Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic Acid</td>
<td>CO₂</td>
</tr>
<tr>
<td>Run no.</td>
<td>68</td>
<td>71</td>
</tr>
<tr>
<td>Product found, mmol.</td>
<td>6.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>

I. Calculated values for consumed ClO₂:
- ClO₂ required for product formation, mmol.
- Total ClO₂ required, mmol.
- ClO₂ consumed, mmol.
- Excess consumed ClO₂ over total required ClO₂, mmol.

<table>
<thead>
<tr>
<th></th>
<th>1.3</th>
<th>2.2</th>
<th>2.7</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.5</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

II. Calculated values for consumed starting organic compound:
- Starting organic compound required for product formation, mmol.
- Total starting organic compound required, mmol.
- Starting organic compound added, mmol.
- Starting organic compound recovered unchanged, mmol.
- Starting organic compound unaccounted for, mmol.

<table>
<thead>
<tr>
<th></th>
<th>3.2</th>
<th>0.6</th>
<th>2.3</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.8</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>10.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>7.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
in physical chemistry. Many free radical reactions, however, have been shown to proceed by zero order mechanisms. Free radicals are defined as molecules or atoms having an odd number of electrons which produce an unbalanced electron spin and, thereby, permanent magnetic moments. Electron diffraction studies of chlorine dioxide in the gas phase have shown that the chlorine dioxide molecule can be represented mainly by the following double bonded structure:

\[
\begin{align*}
\text{O}=\text{Cl} & \quad \text{O} \\
\end{align*}
\]

Therefore, the structure of the chlorine dioxide molecule fits the definition presented for a free radical and, consequently, a free radical reaction mechanism could be a possible explanation of these zero order reaction rates. No experimental proof for this hypothesis can be presented, however, since the mechanism of the possible free radical formation in aqueous solution is not known.

The two successive apparent zero order reactions measured for the oxidation of n-butyraldehyde at pH 1 can be explained as resulting from the rapid formation of n-butyric acid followed by the slower formation of carbon dioxide. Only a single reaction rate could be determined for each of the other compounds, however. This result could originate from the fact (1) that only the initial reaction in which the acid is formed was rapid enough to be measured, or (2) that the rates of formation of the two reaction products are not sufficiently different to allow their separate determination.
The formation of acetic acid during the oxidations of diacetyl and 2,3-butanediol shows that chlorine dioxide is a sufficiently strong oxidizing agent to cleave carbon-carbon bonds. This result was expected because the presence of carbonyl and hydroxyl groups on the C₂ and C₃ positions would make these positions more liable to oxidative attack. Three other oxidizing agents—peracetic acid (22), periodic acid (23), and calcium hypochlorite (24)—have also been shown to produce acetic acid from diacetyl.

The formation of carbon dioxide during these oxidations is probably the result of chlorine dioxide attack upon the carboxylic acid formed during the oxidation. If this is the case, hydroxyl, carbonyl, and carboxyl groups are unstable in chlorine dioxide solutions at pH 1. This oxidation of molecules containing carboxyl groups was unexpected because, generally, such oxidations of the lower fatty acids have been found to be difficult (25-27).

The stability of the various functional groupings toward chlorine dioxide attack at pH 1 can be ranked in the following order: primary alcohol > α-glycol > α-hydroxyketone > α-diketone > aldehyde. Essentially the same ranking order seems to also hold for oxidations at pH 7. Since tentative evidence has been presented to show that the α-glycol grouping is oxidized to the α-diketone grouping before the molecule is cleaved to form acetic acid, it is likely that the α-hydroxyketone grouping also would be oxidized to the α-diketone grouping before this molecule is cleaved. Since, in general, the nonspecific oxidation of a hydroxyl group is more easily accomplished than cleavage of a carbon-carbon bond, it would appear anomalous that the α-hydroxyketone is more stable to attack than the α-diketone.
Diacetyl, however, dissociates readily to acetyl free radicals in the presence of light (28). Since chlorine dioxide molecules are free radicals, this same dissociation could occur in their presence. Once acetyl free radicals have been formed, they should be readily oxidizable to acetic acid, thereby explaining the more rapid oxidation of the α-diketone.

The results from the kinetic and reaction product studies on the oxidations of these simple compounds may be related to the possible chlorine dioxide oxidation of cellulose in the following ways:

1. Carbonyl groups were found to react more readily with chlorine dioxide than hydroxyl groups at both pH 1 and 7. This observation correlates directly with the slight cellulose degradation produced by chlorine dioxide on a normally bleached pulp and the marked degradation of an overbleached pulp.

2. Carbonyl compounds were found to react readily with chlorine dioxide at pH 7, while hydroxyl compounds did not react at this pH. This result would mean that during chlorine dioxide bleaches near the neutral point, the reaction with cellulose should be limited primarily to those points in the anhydroglucose chain which had already been oxidized to carbonyl groups in the previous bleaching steps. Therefore, if the previous bleaching operations have not damaged the pulp, there should be little cellulose attack near pH 7.

3. Hydroxyl groups were found to be stable to chlorine dioxide attack at pH 7 but were oxidized slowly at pH 1. Consequently, more oxidative attack on the hydroxyl groups in cellulose could be expected as the bleach liquor pH decreases.
4. Acetic acid and carbon dioxide were isolated as reaction products from the oxidations of diacetyl and 2,3-butanediol. This cleavage of carbon-carbon bonds during cellulose oxidations would result in the formation of carboxyl groups at the C$_2$ and C$_3$ positions in the anhydroglucose chains.
CONCLUSIONS

1. The general aspects of the chlorine dioxide oxidations studied include:
   a. Chlorine dioxide solutions buffered at pH 7 (mono-dipotassium phosphate buffer) are unstable. Solutions buffered at pH 1 (nitric acid-potassium nitrate buffer), however, are stable.
   b. While buffer catalysis effects were very prominent with each compound oxidized at pH 7, no such effect was found with oxidations at pH 1.
   c. Surface area was found to have no effect upon the rate of reaction at pH 1.

2. The stability of the functional groupings toward chlorine dioxide attack at pH 1 can be ranked in the following order: primary alcohol > α-glycol > α-hydroxyketone > α-diketone > aldehyde. Essentially the same ranking order appears to hold at pH 7. The hydroxyl compounds, however, react more readily at the same temperature with chlorine dioxide at pH 1 than at pH 7 while the reverse is true for the carbonyl compounds.

3. All reaction mechanisms for oxidations at pH 1 are apparently zero order with respect to chlorine dioxide consumption, and there are indications that the same is true at pH 7.

4. The activation energies and temperature coefficients calculated from the rate constants for pH 1 oxidations were of the magnitude expected for reactions occurring under these experimental conditions.
5. The isolation of acetic acid and carbon dioxide as reaction products from the oxidations of diacetyl and 2,3-butanediol at pH 1 shows that there is appreciable chain cleavage during these oxidations of C_4 compounds to C_2 and C_1 fragments.

6. The two successive reactions noted in the oxidation of n-butyraldehyde at pH 1 can be explained on the basis of the formation of n-butyric acid followed by the formation of carbon dioxide.

7. The isolation of a small amount of carbonyl material from the oxidation of 2,3-butanediol which appears to contain diacetyl indicates that the α-glycol is oxidized to diacetyl before the molecule is cleaved to form two molecules of acetic acid.
LITERATURE CITED


APPENDIX I

PREPARATION AND ANALYSIS OF AQUEOUS CHLORINE DIOXIDE SOLUTIONS

Chlorine dioxide was prepared by passing a controlled mixture of chlorine gas and air through two sodium chlorite (technical grade) beds as illustrated in Figure 12. The unreacted chlorine was removed by bubbling the gas mixture through a saturated barium hydroxide solution (29, 30). The purified gas mixture was then bubbled through triple distilled water containing 3 ml. of 1N nitric acid per liter to produce the chlorine dioxide solution. This procedure is a modification of Pulping Group Procedure 74 of The Institute of Paper Chemistry.

This chlorine dioxide solution was analyzed iodometrically for chlorine dioxide and chlorine by the neutral and acid titration method of Giertz (31):

Twenty milliliters of the liquor was transferred into a mixture of 100 ml. of water, 2 g. potassium iodide crystals, and 20 ml. of buffer solution (100 g. of dipotassium phosphate dissolved in 450 ml. of water and adjusted to a pH of 7.0-7.5 with phosphoric acid). The sample was immediately titrated with 0.1N sodium thiosulfate using Thymene indicator near the end point. The amount of thiosulfate consumed (ml.) = $T_n$. Twenty milliliters of 4N sulfuric acid was added and after 3 minutes the titration was continued. The total amount of sodium thiosulfate consumed (ml.) in the titration = $T_s$. (Since the acidic titration was a direct continuation of the neutral one, the $T_n$ value also entered into the $T_s$ value.)

The neutral titration corresponds to 1/5 of the oxidizing equivalent of
chlorine dioxide, and the chlorine reacts quantitatively. The additional amount of thiosulfate consumed in the acidic titration corresponded to \(\frac{4}{5}\) of the oxidizing equivalents of chlorine dioxide. Thus, \(\text{ClO}_2 = \frac{5}{4} (T_s - T_n)\) and g./l. \(\text{ClO}_2 = 1.688 (T_s - T_n)\) (normality of sodium thiosulfate).

\(\text{Cl}_2 = T_s - \frac{5}{4} (T_s - T_n)\) and g./l. \(\text{Cl}_2 = (3.55) [T_s - \frac{5}{4}(T_s - T_n)]\) (normality of sodium thiosulfate). If no \(\text{Cl}_2\) was present, \(T_s = \frac{5}{4}(T_s - T_n)\).
Figure 12. Block Diagram of Chlorine Dioxide Generation and Purification Equipment
APPENDIX II

QUANTITATIVE TRANSFER OF CHLORINE DIOXIDE SOLUTIONS

Quantitative transfer of aqueous chlorine dioxide solutions was accomplished with the apparatus illustrated in Figure 13. This transfer device was operated in the following manner:

1. The bath temperature was controlled at the oxidation temperature with a Fenwal Thermostwitch.

2. Purified chlorine dioxide solution was added to both flasks. The solution level in the small flask was kept above the bottom of the air inlet tube.

3. The buret was then filled by applying a slight positive pressure to the air inlet tube after closing the stopcock below the Bunsen valve and opening the three-way vent stopcock to both the atmosphere, and the buret. The level of the solution in the buret was controlled by the source stopcock.

4. The three-way vent stopcock was then closed to the atmosphere. The stopcock below the Bunsen valve was opened while the chlorine dioxide solution reached bath temperature in order to relieve any pressure formed because of temperature change. This stopcock was closed thereafter only when chlorine dioxide solution was being removed.

5. When the chlorine dioxide solution reached the bath temperature (about 2 hours), the buret was rinsed and then the correct sample volume for chlorine dioxide analysis or reaction mixture preparation was measured from the buret.

This transfer device makes it possible to transfer chlorine dioxide
solutions quantitatively because all air entering the system is first bubbled through a chlorine dioxide solution of the same concentration and temperature as the solution being transferred. In this manner, the air above the solution being transferred is kept essentially saturated with chlorine dioxide at all times, thus minimizing losses.
Figure 13. Quantitative Transfer Device for Aqueous Chlorine Dioxide Solutions
APPENDIX III

GAS CHROMATOGRAPHY APPARATUS

Gas chromatography offered both a fast and an efficient analysis technique for organic materials because both the starting organic compounds and the expected reaction products were volatile. The relatively small amount of organic starting materials and reaction products which would be present in a relatively large volume of Freon-TF solvent, however, required that the column be of relatively large diameter. Consequently, a gas chromatography apparatus was constructed which used 1/2-in. inner diameter (i.d.) glass columns capable of handling 0.50-ml. samples. A diagram of this apparatus is presented in Figure 14.

PHYSICAL COMPONENTS

The details of the physical components of this apparatus are listed below:

1. **Helium Cylinder.** The helium was research-grade helium (99.99%) obtained from The Matheson Company, Inc.

2. **Reducing Valve.** The reducing valve was a double dial single stage regulator attached to the helium cylinder.

3. **Drying Column.** Any moisture present in the helium was removed in a 12-in. length of 2-in. galvanized pipe filled with silica gel. The caps at each end of the pipe were tapped and fitted with compression fittings to allow passage of the helium.

4. **Flow Rate Controller.** A controller as described by James and Phillips (32) was constructed to control flow rate. It was generally found,
Figure 14. Block Diagram of Gas Chromatography Apparatus

- ROTAMETER
- MANIFOLD FRACTION COLLECTOR
- RECORDER
- AMPLIFIER
- CHOPPER
- SAMPLE
- GAS ANALYSIS CELL
- PRE-HEATER
- COLUMN
- FLOW RATE CONTROLLER
- PRESSURE GAGE
- DRYING COLUMN
- REDUCING VALVE
- HELIUM CYLINDER
- CONSTANT TEMPERATURE BATH
however, that flow rate variations were small enough so that it was not necessary to use this device.

5. **Pressure Gage.** Column pressure was determined by the reading of an Ashcroft pressure gage AMP-7440, 0-30 p.s.i., corrected to read to within ±0.2 p.s.i.

6. **Constant Temperature Bath.** The constant temperature bath was a 30-gallon drum filled with Socony-Vacuum Etna Oil Extra Heavy—flash point 490°F., viscosity 500 sec. at 100°F. (Sayboldt). The bath temperature was controlled by a mercury thermoregulator (No. S-81840, E.H. Sargent and Company) to about ±0.05°C. The bath was heated by two 1350 w., 220 v. Chromalox tubular elements (No. ATU-2113, 3/8-in. size, 21-in. length, Gordon Hatch Company). One of these heaters was operated by the thermostat while the other was operated manually. The bath was stirred with a Lightnin' mixer (Model CV-2, 1/8 h.p., variable speed, Mixing Equipment Company, Inc.).

7. **Connectors.** All tubing connections inside the bath with the exception of those on the column were made with stainless steel couplings consisting of a double-ended threaded packing gland. Teflon O-rings were used as the packing medium with the threaded glands exerting axial pressure on the rings.

8. **Preheater.** The preheater was a length of 1/4-in. copper tubing running to the bottom of the bath and then back up to the gas analysis cell. This length of tubing allows the temperature of the helium to equilibrate with that of the bath before entering the gas analysis cell.

9. **Gas Analysis Cell.** This cell consists of two matched thermistor beads mounted in the two channels of a stainless steel block. The reference
bead was mounted in the stream of entering helium while the detector bead was mounted in the helium stream from the column.

10. **Sampler.** Samples to be analyzed were injected through a rubber perforation disk (No. 8826, size 11, Arthur H. Thomas) with a 1-ml. tuberculin syringe (No. 1 YT, Becton-Dickinson and Company) into a chamber filled with glass wool. This chamber was located inside a stainless steel cylinder which was connected to the column with a 28/12 stainless steel outer socket joint. Helium entered the chamber from the side near the top and flowed down through the glass wool into the column.

11. **Column.** The column consisted of a series of 1/2-in. i.d. glass U-tubes 18 in. long. The arms of the tubes were separated 2 in. and each end was equipped with a 28/12 inner ball joint. Up to six of these U-tubes have been used in one column. The U-tubes were connected by glass connectors consisting of two 28/12 outer socket joints arranged in U-shape which were separated 2 in. by 3-mm. i.d. glass tubing. The tubes were connected together inside the bath on the circumference of a circle to form the column. The 28/12 ball and socket joints were sealed with Dow-Corning No. 11 Compound and were held together with screw-type clamps (No. C 5155, A. Daigger and Company).

12. **Manifold Fraction Collector.** The fractions separated from the sample were isolated on a double manifold system. Each manifold consisted of two 6-mm. V-bore stopcocks which were turned to divert the gas stream into a glass U-shaped collection tube when a fraction was collected. These collection tubes had an 8-mm. outside diameter (o.d.) entrance arm and 4-mm. o.d. exit arm and were immersed in a dry ice-ethanol bath to freeze out the
fraction. The tubing carrying the gases to the manifold system as well as the manifold system itself was heated electrically by wrapping with nichrome wire and was insulated with asbestos string to prevent premature condensation.

13. Rotameter. The helium flow rate through the column was determined with a variable area flowmeter (Tri-flat tube no. 08F 1/16-16-4/35, sapphire float, standard taper ground glass joints, Fischer & Porter Company).

**DETECTION COMPONENTS**

The presence of materials injected into the gas chromatography apparatus in the helium gas stream was detected by measuring the unbalance of a Wheatstone bridge circuit containing the gas analysis cell. A detailed diagram of this circuit is presented in Figure 15.

The details of the components of this system are listed below:

1. **Gas Analysis Cell.** This cell was a thermistor-bead type thermal conductivity cell, Victory Engineering Corporation Gas Analysis Cell M 182 with seals modified to withstand 100 p.s.i. and 100°C. It was labeled Gas Analysis Cell VECO Type MX 210 Serial 1.

2. **Chopper.** The direct current (d.c.) signal from the bridge circuit was a chopper (Stevens-Arnold catalog A-12) modulated so that it could be amplified by the alternating current (a.c.) Densichron amplifier. The chopper, however, was modified so that the time the contacts were closed was equal to the time they were open. This modification resulted in a symmetrical square wave output better suited for application to the Densichron for amplification.
3. **Amplifier.** The Densichron is a 120-cycle a.c. amplifier. To minimize changes in amplifier output due to changes in line voltage, it was operated from an a.c. voltage regulator (Model 150-S, Sorenson and Company, Inc.).

4. **Recorder.** Signals from the amplifier were recorded by an Esterline-Angus Direct Current Graphic Ammeter Model AW. The current sensitivity of this recorder was 1.0 milliamperes d.c. for full scale deflection.

**COLUMN PREPARATION**

Selection of a column packing to separate a particular mixture must be done primarily by a trial and error procedure. Graded (30-60 mesh) C-22 diatomaceous earth firebrick (No. 11-130-50, Fisher Scientific Company) was chosen as support material because of its relatively low flow resistance. Many different liquids were used to find one that would give the desired separation.

Column packings were prepared by the following method: the desired amount of liquid phase was dissolved in a suitable solvent and applied to the support material. This solvent was evaporated with stirring on a steam bath and the last traces of solvent removed by drying overnight in a vacuum oven at 60°C.

Purification of the support material by the method of James and Martin (32) to minimize adsorption effects was found to have no effect upon the experimental results and, consequently, was abandoned. Table XI lists the components, amounts, and solvents for each of the column packings prepared.
TABLE XI

DETAILS OF COLUMN PACKINGS PREPARED WITH CRUSHED C-22 FIREBRICK SUPPORT MATERIAL

<table>
<thead>
<tr>
<th>Column Liquid</th>
<th>Liquid Content, % (w/w)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbowax 1500 Poly-ethylene Glycol</td>
<td>29</td>
<td>Methanol</td>
</tr>
<tr>
<td>DC Silicone 710 Fluid</td>
<td>29</td>
<td>Absolute Ether</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>40</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Di-2-Ethyl Hexyl Phthalate</td>
<td>40</td>
<td>Acetone</td>
</tr>
<tr>
<td>Tetraethylene Glycol Dimethyl Ether</td>
<td>30</td>
<td>Acetone</td>
</tr>
<tr>
<td>Tri-m-Tolyl Phosphate</td>
<td>26</td>
<td>Methanol</td>
</tr>
<tr>
<td>Diglycerol</td>
<td>{30}</td>
<td>{20}</td>
</tr>
<tr>
<td>Bis (2-Methoxyethyl) Phthalate</td>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td>DC Silicone High Vacuum Grease</td>
<td>9</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Carbowax 1250 Methoxy Polyethylene Glycol</td>
<td>20</td>
<td>Methanol</td>
</tr>
<tr>
<td>Purified DC Silicone High Vacuum Grease (3A)</td>
<td>20</td>
<td>Chloroform</td>
</tr>
</tbody>
</table>
The only column packing capable of separating small amounts of acetic acid in the mixtures of interest was the DC Silicone 710 Fluid packing.

Each U-tube section of the column was packed by adding the coated brick preparation in small amounts to each side of the tube and tapping down lightly with a glass rod.

OPERATION

The apparatus should run about ten hours at the desired temperature, bridge voltage, and helium flow rate before an analysis was begun. This time was required for the bridge circuit to produce a uniform, constant signal. Since this long warm-up period required starting the apparatus on one day and doing the analysis the next, the bath was maintained at temperature and the bridge was left on overnight. The flow of helium, however, was stopped. Upon starting the flow of helium the next morning, the system was ready for an analysis in about two hours.

From the existing atmospheric temperature and pressure, the volume correction for the rotameter was determined from Figure 16. This factor was multiplied by the desired helium flow rate and the rotameter reading corresponding to this corrected flow rate was determined from Figure 17. The needle valve on the helium cylinder was then adjusted to give this rotameter reading. Now, when the signal from the bridge circuit became constant, an analysis was started.

A known volume of sample was injected from a tuberculin syringe. The appearance of a small air blip indicated zero time. The Densichron
amplification setting was varied during the analysis to accommodate the various peaks on the recorder strip chart.

The peaks of interest were separated by moving the manifold fraction collector stopcocks at the proper time so that the desired fraction was diverted into a U-tube immersed in a dry ice-ethanol mixture. When the fraction was collected, the stopcocks were returned to the by-pass position and the U-tube was removed from the fraction collector and stoppered immediately. A known volume of the desired infrared solvent (carbon tetrachloride or chloroform) was then added to the tube and the tube was warmed to room temperature. The infrared spectrum of this solution was run against that of the solvent on a Perkin-Elmer Model 21 Recording Spectrophotometer. The identity of the material separated by the gas chromatography apparatus was determined from this spectrum. Quantitative results were also obtained from these spectra by the use of previously determined Beer's law curves (curves for diacetyl and 2,3-butanediol presented in Figure 3 and Figure 4, respectively). The concentration of this separated material in the original sample can then be calculated when solvent and sample volumes are known.
Figure 16. Flowrator Correction Curve for Atmospheric Conditions
Figure 17. Calibration Curve for Fisher and Porter Flowrator Tube No. 08F 1/16-16-4/35

MEASURED AT 23°C AND 740 MM. Hg
APPENDIX IV

KINETIC DATA AT pH 7

The data upon which the kinetics observations at pH 7 are based are presented in Table XII for blank solutions, Table XIII for diacetyl, Table XIV for acetoin, and Table XV for acetaldehyde, ethanol, and 2,3-butanediol.
<table>
<thead>
<tr>
<th>Run no.</th>
<th>28A</th>
<th>34A</th>
<th>35A</th>
<th>44A</th>
<th>47A</th>
<th>52A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic compound</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Temperature, °C.</td>
<td>30.2</td>
<td>20.00 ± 0.03</td>
<td>10.00 ± 0.02</td>
<td>40.00 ± 0.02</td>
<td>70.00 ± 0.05</td>
<td>80.00 ± 0.05</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Initial concentration</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Organic compound</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ClO₂</td>
<td>0.0100 M</td>
<td>0.0100 M</td>
<td>0.0100 M</td>
<td>0.0100 M</td>
<td>0.0100 M</td>
<td>0.0069 M</td>
</tr>
<tr>
<td>H₂PO₄⁻·HPO₄²⁻ buffer volume, ml</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Total volume, ml</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Reaction mixture density, g/ml</td>
<td>1,064</td>
<td>1,064</td>
<td>1,065</td>
<td>1,087</td>
<td>1,085</td>
<td>1,086</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Conc. (g/ml)</th>
<th>Time (minutes)</th>
<th>Conc. (g/ml)</th>
<th>Time (minutes)</th>
<th>Conc. (g/ml)</th>
<th>Time (minutes)</th>
<th>Conc. (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>42.5</td>
<td>17</td>
<td>43.8</td>
<td>53</td>
<td>44.8</td>
<td>12</td>
<td>36.3</td>
</tr>
<tr>
<td>20</td>
<td>38.7</td>
<td>17</td>
<td>45.5</td>
<td>53</td>
<td>28.2</td>
<td>17</td>
<td>30.3</td>
</tr>
<tr>
<td>29</td>
<td>36.6</td>
<td>26</td>
<td>46.8</td>
<td>58</td>
<td>28.2</td>
<td>17</td>
<td>30.3</td>
</tr>
<tr>
<td>80</td>
<td>30.0</td>
<td>17</td>
<td>39.3</td>
<td>74</td>
<td>26.4</td>
<td>17</td>
<td>30.3</td>
</tr>
<tr>
<td>100</td>
<td>28.7</td>
<td>18</td>
<td>35.9</td>
<td>96</td>
<td>26.4</td>
<td>17</td>
<td>30.3</td>
</tr>
<tr>
<td>166</td>
<td>25.8</td>
<td>179</td>
<td>30.7</td>
<td>178</td>
<td>23.0</td>
<td>196</td>
<td>20.9</td>
</tr>
<tr>
<td>185</td>
<td>25.4</td>
<td>205</td>
<td>29.4</td>
<td>228</td>
<td>22.2</td>
<td>228</td>
<td>20.9</td>
</tr>
<tr>
<td>215</td>
<td>25.0</td>
<td>234</td>
<td>28.5</td>
<td>256</td>
<td>22.2</td>
<td>228</td>
<td>20.9</td>
</tr>
<tr>
<td>247</td>
<td>23.8</td>
<td>261</td>
<td>27.8</td>
<td>289</td>
<td>22.2</td>
<td>256</td>
<td>20.7</td>
</tr>
<tr>
<td>288</td>
<td>23.6</td>
<td>292</td>
<td>27.2</td>
<td>272</td>
<td>22.3</td>
<td>247</td>
<td>20.7</td>
</tr>
</tbody>
</table>

\(^{a}\) Time in minutes

\(^{b}\) Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
### TABLE XIII
Experimental Data for Diacetyl Oxidations at pH 7

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C.</th>
<th>pH</th>
<th>Initial concentration</th>
<th>Organic compound</th>
<th>Chlorite</th>
<th>H₂PO₄⁻/K₂HPO₄ buffer volume, ml.</th>
<th>Total volume, ml.</th>
<th>Volume Na₂SO₃, ml.</th>
<th>Reaction mixture density, g./ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>-</td>
<td>1.065</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>60</td>
<td>200</td>
<td>-</td>
<td>1.085</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>60</td>
<td>200</td>
<td>-</td>
<td>1.074</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>60</td>
<td>200</td>
<td>-</td>
<td>1.059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>-</td>
<td>1.085</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>33.8</td>
<td>9</td>
<td>40.8</td>
<td>8</td>
<td>43.8</td>
<td>11</td>
<td>43.1</td>
<td>8</td>
<td>42.0</td>
<td>8</td>
<td>43.2</td>
</tr>
<tr>
<td>19</td>
<td>30.4</td>
<td>18</td>
<td>36.3</td>
<td>17</td>
<td>40.5</td>
<td>21</td>
<td>39.2</td>
<td>17</td>
<td>37.2</td>
<td>8</td>
<td>37.2</td>
</tr>
<tr>
<td>28</td>
<td>27.8</td>
<td>57</td>
<td>23.1</td>
<td>37</td>
<td>34.1</td>
<td>58</td>
<td>26.6</td>
<td>36</td>
<td>29.6</td>
<td>36</td>
<td>29.6</td>
</tr>
<tr>
<td>50</td>
<td>23.6</td>
<td>78</td>
<td>19.8</td>
<td>57</td>
<td>28.9</td>
<td>78</td>
<td>24.1</td>
<td>56</td>
<td>23.3</td>
<td>56</td>
<td>23.3</td>
</tr>
<tr>
<td>134</td>
<td>19.3</td>
<td>151</td>
<td>18.4</td>
<td>131</td>
<td>19.2</td>
<td>97</td>
<td>21.2</td>
<td>74</td>
<td>20.3</td>
<td>74</td>
<td>20.3</td>
</tr>
<tr>
<td>153</td>
<td>18.4</td>
<td>176</td>
<td>18.0</td>
<td>156</td>
<td>18.3</td>
<td>171</td>
<td>18.6</td>
<td>147</td>
<td>18.4</td>
<td>147</td>
<td>18.4</td>
</tr>
<tr>
<td>183</td>
<td>17.7</td>
<td>210</td>
<td>17.4</td>
<td>189</td>
<td>17.8</td>
<td>199</td>
<td>17.8</td>
<td>176</td>
<td>18.1</td>
<td>176</td>
<td>18.1</td>
</tr>
<tr>
<td>215</td>
<td>17.9</td>
<td>255</td>
<td>18.0</td>
<td>239</td>
<td>17.1</td>
<td>241</td>
<td>17.4</td>
<td>218</td>
<td>17.4</td>
<td>218</td>
<td>17.4</td>
</tr>
<tr>
<td>248</td>
<td>16.9</td>
<td>296</td>
<td>16.0</td>
<td>276</td>
<td>16.1</td>
<td>278</td>
<td>16.6</td>
<td>255</td>
<td>16.9</td>
<td>255</td>
<td>16.9</td>
</tr>
</tbody>
</table>

---

*Time in minutes

b Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
### Table XIV

**Experimental Data for Acetoin Oxidations at pH 7**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C.</th>
<th>pH</th>
<th>Initial concentration</th>
<th>Organic compound</th>
<th>Citrate</th>
<th>H$_2$PO$_4$-KH$_2$PO$_4$ buffer</th>
<th>Total volume, mL</th>
<th>Reaction mixture density, g./ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>28B</td>
<td>Acetoin</td>
<td>30.2</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>1.064</td>
</tr>
<tr>
<td>41B</td>
<td>Acetoin</td>
<td>40.00 ± 0.02</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>1.085</td>
</tr>
<tr>
<td>47B</td>
<td>Acetoin</td>
<td>50.00 ± 0.05</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>1.085</td>
</tr>
<tr>
<td>48A</td>
<td>Acetoin</td>
<td>50.00 ± 0.05</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>1.062</td>
</tr>
<tr>
<td>48B</td>
<td>Acetoin</td>
<td>50.00 ± 0.05</td>
<td>7.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>90</td>
<td>200</td>
<td>1.085</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>41.9</td>
<td>8</td>
<td>40.2</td>
<td>9</td>
<td>33.5</td>
<td>7</td>
<td>37.2</td>
<td>7</td>
<td>35.0</td>
<td>17</td>
<td>30.2</td>
</tr>
<tr>
<td>17</td>
<td>38.6</td>
<td>19</td>
<td>33.6</td>
<td>18</td>
<td>26.4</td>
<td>17</td>
<td>30.2</td>
<td>17</td>
<td>27.8</td>
<td>35</td>
<td>21.4</td>
</tr>
<tr>
<td>27</td>
<td>35.8</td>
<td>38</td>
<td>27.2</td>
<td>48</td>
<td>19.8</td>
<td>54</td>
<td>20.0</td>
<td>55</td>
<td>19.0</td>
<td>84</td>
<td>17.1</td>
</tr>
<tr>
<td>47</td>
<td>32.0</td>
<td>61</td>
<td>23.6</td>
<td>67</td>
<td>17.9</td>
<td>74</td>
<td>18.6</td>
<td>84</td>
<td>17.1</td>
<td>177</td>
<td>16.2</td>
</tr>
<tr>
<td>66</td>
<td>28.8</td>
<td>141</td>
<td>19.0</td>
<td>87</td>
<td>16.6</td>
<td>102</td>
<td>16.4</td>
<td>176</td>
<td>16.2</td>
<td>223</td>
<td>16.1</td>
</tr>
<tr>
<td>132</td>
<td>23.8</td>
<td>160</td>
<td>18.5</td>
<td>184</td>
<td>16.0</td>
<td>195</td>
<td>15.6</td>
<td>177</td>
<td>16.2</td>
<td>223</td>
<td>16.1</td>
</tr>
<tr>
<td>150</td>
<td>22.8</td>
<td>188</td>
<td>17.9</td>
<td>210</td>
<td>15.9</td>
<td>241</td>
<td>15.1</td>
<td>223</td>
<td>16.1</td>
<td>279</td>
<td>16.1</td>
</tr>
<tr>
<td>181</td>
<td>21.9</td>
<td>224</td>
<td>17.4</td>
<td>244</td>
<td>15.7</td>
<td>298</td>
<td>15.3</td>
<td>279</td>
<td>16.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>20.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>251</td>
<td>19.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*Time in minutes*

*Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)*
### TABLE XV

**EXPERIMENTAL DATA FOR ACETALDEHYDE, ETHANOL, AND 2,3-BUTANEDIOL OXIDATIONS AT pH 7**

<table>
<thead>
<tr>
<th>Run no</th>
<th>Organic compound</th>
<th>Temperature, °C</th>
<th>pH</th>
<th>Initial concentration</th>
<th>Temperature, °C</th>
<th>pH</th>
<th>Initial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>34B</td>
<td>AcH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20.00 ± 0.03</td>
<td>7.0</td>
<td>0.0200M</td>
<td>20.00 ± 0.03</td>
<td>7.0</td>
<td>0.0200M</td>
</tr>
<tr>
<td>38A</td>
<td>AcH</td>
<td>10.00 ± 0.02</td>
<td>7.0</td>
<td>0.0083M</td>
<td>10.00 ± 0.05</td>
<td>7.0</td>
<td>0.0083M</td>
</tr>
<tr>
<td>38B</td>
<td>AcH</td>
<td>10.00 ± 0.05</td>
<td>7.0</td>
<td>0.0100M</td>
<td>10.00 ± 0.05</td>
<td>7.0</td>
<td>0.0100M</td>
</tr>
<tr>
<td>52B</td>
<td>Diol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>52B</td>
<td>7.0</td>
<td>0.0100M</td>
<td>52B</td>
<td>7.0</td>
<td>0.0069M</td>
</tr>
</tbody>
</table>

| H<sub>2</sub>PO<sub>4</sub>, 2K<sub>2</sub>HPO<sub>4</sub> buffer | volume, ml. | 90 | 60 | 90 | 90 | 90 |
| Total volume, ml.                                                                 | 200          | 200 | 200 | 200 | 200 |

| Reaction mixture density, g/cm<sup>3</sup> | 1.064 | 1.062 | 1.084 | 1.090 | 1.086 |

<table>
<thead>
<tr>
<th>Time&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>36.2</td>
<td>9</td>
<td>31.3</td>
<td>9</td>
<td>27.1</td>
<td>8</td>
<td>16.2</td>
<td>8</td>
<td>13.0</td>
<td>17</td>
<td>12.9</td>
</tr>
<tr>
<td>17</td>
<td>32.0</td>
<td>18</td>
<td>30.2</td>
<td>20</td>
<td>32.5</td>
<td>17</td>
<td>14.2</td>
<td>17</td>
<td>10.9</td>
<td>36</td>
<td>10.8</td>
</tr>
<tr>
<td>26</td>
<td>32.2</td>
<td>49</td>
<td>29.1</td>
<td>40</td>
<td>28.1</td>
<td>44</td>
<td>12.5</td>
<td>36</td>
<td>10.9</td>
<td>10.9</td>
<td>10.3</td>
</tr>
<tr>
<td>44</td>
<td>26.8</td>
<td>77</td>
<td>27.9</td>
<td>59</td>
<td>26.2</td>
<td>77</td>
<td>12.1</td>
<td>55</td>
<td>10.3</td>
<td>86</td>
<td>10.3</td>
</tr>
<tr>
<td>125</td>
<td>15.1</td>
<td>158</td>
<td>26.2</td>
<td>140</td>
<td>23.9</td>
<td>107</td>
<td>11.7</td>
<td>86</td>
<td>10.3</td>
<td>86</td>
<td>10.3</td>
</tr>
<tr>
<td>244</td>
<td>12.3</td>
<td>185</td>
<td>21.7</td>
<td>165</td>
<td>20.1</td>
<td>151</td>
<td>11.6</td>
<td>113</td>
<td>10.0</td>
<td>145</td>
<td>9.9</td>
</tr>
<tr>
<td>170</td>
<td>11.6</td>
<td>216</td>
<td>20.8</td>
<td>196</td>
<td>17.6</td>
<td>200</td>
<td>11.9</td>
<td>187</td>
<td>9.7</td>
<td>227</td>
<td>9.6</td>
</tr>
<tr>
<td>199</td>
<td>8.5</td>
<td>263</td>
<td>17.1</td>
<td>245</td>
<td>15.2</td>
<td>187</td>
<td>9.7</td>
<td>187</td>
<td>9.7</td>
<td>227</td>
<td>9.6</td>
</tr>
<tr>
<td>225</td>
<td>8.3</td>
<td>306</td>
<td>16.5</td>
<td>285</td>
<td>15.5</td>
<td>227</td>
<td>9.6</td>
<td>227</td>
<td>9.6</td>
<td>227</td>
<td>9.6</td>
</tr>
<tr>
<td>257</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Acetaldehyde

<sup>b</sup> 2,3-Butanediol

<sup>c</sup> Time in minutes

<sup>d</sup> Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
APPENDIX V

KINETIC DATA AT pH 1

The data upon which the kinetics observations at pH 1 are based are presented in Table XVI for ethanol, Table XVII for 2,3-butanediol, Table XVIII and Table XIX for acetoin, Table XX for diacetyl, and Table XXI for blank and n-butyraldehyde.
### TABLE XVI

**EXPERIMENTAL DATA FOR ETHANOL OXIDATIONS AT pH 1**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C.</th>
<th>pH</th>
<th>Initial concentration</th>
<th>Organic compound</th>
<th>ClO₂</th>
<th>HNO₃ = KNO₃ buffer</th>
<th>volume, ml.</th>
<th>Total volume, ml.</th>
<th>Reaction mixture density, g./ml.</th>
<th>Time</th>
<th>Conc. b</th>
</tr>
</thead>
<tbody>
<tr>
<td>55A</td>
<td>Ethanol</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0070M</td>
<td>50</td>
<td>200</td>
<td>1.024</td>
<td>69</td>
<td></td>
<td>8</td>
<td>33.2</td>
</tr>
<tr>
<td>55B</td>
<td>Ethanol</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0070M</td>
<td>40</td>
<td>200</td>
<td>1.022</td>
<td>69</td>
<td></td>
<td>18</td>
<td>33.7</td>
</tr>
<tr>
<td>59A</td>
<td>Ethanol</td>
<td>70.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0084M</td>
<td>50</td>
<td>200</td>
<td>1.025</td>
<td>74</td>
<td></td>
<td>55</td>
<td>32.8</td>
</tr>
<tr>
<td>51B</td>
<td>Ethanol</td>
<td>80.5</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>50</td>
<td>200</td>
<td>1.022</td>
<td>80</td>
<td></td>
<td>9</td>
<td>42.2</td>
</tr>
</tbody>
</table>

**a** Time in minutes  
**b** Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C.</th>
<th>pH</th>
<th>Initial concentration</th>
<th>ΔClO₂</th>
<th>HNO₃ ± KNO₃ buffer</th>
<th>Total volume, ml.</th>
<th>Reaction mixture density, g./ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50B</td>
<td>80.5</td>
<td>1.0</td>
<td>0.010M</td>
<td>0.0100M</td>
<td>200</td>
<td>1.025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54A</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0080M</td>
<td>200</td>
<td>1.024</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54B</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0080M</td>
<td>200</td>
<td>1.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59B</td>
<td>70.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0083M</td>
<td>200</td>
<td>1.025</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>41.3</td>
<td>8</td>
<td>38.9</td>
<td>8</td>
<td>38.5</td>
<td>7</td>
<td>40.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>40.1</td>
<td>17</td>
<td>38.4</td>
<td>19</td>
<td>37.4</td>
<td>17</td>
<td>40.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>39.2</td>
<td>57</td>
<td>36.5</td>
<td>39</td>
<td>36.3</td>
<td>47</td>
<td>38.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>37.7</td>
<td>93</td>
<td>33.7</td>
<td>73</td>
<td>34.3</td>
<td>102</td>
<td>38.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>94</td>
<td>35.3</td>
<td>128</td>
<td>31.5</td>
<td>110</td>
<td>32.3</td>
<td>163</td>
<td>36.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>126</td>
<td>33.8</td>
<td>160</td>
<td>30.2</td>
<td>145</td>
<td>30.8</td>
<td>218</td>
<td>33.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>155</td>
<td>32.6</td>
<td>206</td>
<td>27.6</td>
<td>187</td>
<td>28.5</td>
<td>299</td>
<td>32.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>183</td>
<td>31.2</td>
<td>249</td>
<td>25.0</td>
<td>231</td>
<td>26.3</td>
<td>357</td>
<td>32.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>28.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>419</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>473</td>
<td>28.0</td>
</tr>
</tbody>
</table>

a 2,3-Butanediol  
b Time in minutes  
c Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
### TABLE XVIII

**EXPERIMENTAL DATA FOR ACETOIN OXIDATIONS AT pH 1**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C</th>
<th>pH</th>
<th>Initial concentration</th>
<th></th>
<th>Total volume, ml</th>
<th>Reaction mixture density, g/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>50A</td>
<td>Acetoin</td>
<td>80.5</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0079M</td>
<td>200</td>
<td>1.025</td>
</tr>
<tr>
<td>56A</td>
<td>Acetoin</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0079M</td>
<td>200</td>
<td>1.024</td>
</tr>
<tr>
<td>56B</td>
<td>Acetoin</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0079M</td>
<td>200</td>
<td>1.022</td>
</tr>
<tr>
<td>61A</td>
<td>Acetoin</td>
<td>60.00 ± 0.05</td>
<td>1.0</td>
<td>0.0100M</td>
<td>0.0080M</td>
<td>200</td>
<td>1.026</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>41.3</td>
<td>7</td>
<td>35.2</td>
<td>8</td>
<td>33.3</td>
<td>7</td>
<td>38.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>38.8</td>
<td>17</td>
<td>31.4</td>
<td>16</td>
<td>30.9</td>
<td>16</td>
<td>37.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>27.6</td>
<td>55</td>
<td>20.2</td>
<td>35</td>
<td>24.5</td>
<td>68</td>
<td>34.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>19.4</td>
<td>90</td>
<td>12.4</td>
<td>70</td>
<td>17.0</td>
<td>125</td>
<td>31.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>113</td>
<td>10.6</td>
<td>126</td>
<td>4.0</td>
<td>109</td>
<td>14.0</td>
<td>189</td>
<td>27.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>144</td>
<td>5.0</td>
<td>156</td>
<td>3.6</td>
<td>137</td>
<td>6.7</td>
<td>254</td>
<td>24.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>173</td>
<td>3.5</td>
<td>187</td>
<td>0.9</td>
<td>168</td>
<td>3.4</td>
<td>327</td>
<td>22.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>0.2</td>
<td></td>
<td></td>
<td>195</td>
<td>1.4</td>
<td>378</td>
<td>19.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>427</td>
<td>17.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*a  Time in minutes

b  Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Organic compound</th>
<th>Temperature, °C</th>
<th>pH</th>
<th>Initial concentration</th>
<th>Organic compound</th>
<th>Volume, ml</th>
<th>Total volume, ml</th>
<th>Weight glass fibers, g</th>
<th>Reaction mixture density, g/ml</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetoin</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td></td>
<td>0.0100M</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>1.025</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58A</td>
<td>Acetoin</td>
<td>80.00 ± 0.05</td>
<td>1.0</td>
<td></td>
<td>0.0100M</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>1.025</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58B</td>
<td>Acetoin</td>
<td>60.00 ± 0.05</td>
<td>1.0</td>
<td></td>
<td>0.0088M</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>1.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62A</td>
<td>Acetoin</td>
<td>60.00 ± 0.05</td>
<td>1.0</td>
<td></td>
<td>0.0088M</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>1.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>62B</td>
<td>Acetoin</td>
<td>60.00 ± 0.05</td>
<td>1.0</td>
<td></td>
<td>0.0088M</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>1.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Time in minutes

*b Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
<table>
<thead>
<tr>
<th>Run no.</th>
<th>49B</th>
<th>57A</th>
<th>57B</th>
<th>61B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic compound</td>
<td>Diacetyl</td>
<td>Diacetyl</td>
<td>Diacetyl</td>
<td>Diacetyl</td>
</tr>
<tr>
<td>Temperature, °C.</td>
<td>80.5</td>
<td>80.00 ± 0.05</td>
<td>80.00 ± 0.05</td>
<td>60.00 ± 0.05</td>
</tr>
<tr>
<td>pH</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Initial concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic compound</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
</tr>
<tr>
<td>ClO₂</td>
<td>0.0100M</td>
<td>0.0075M</td>
<td>0.0075M</td>
<td>0.0080M</td>
</tr>
<tr>
<td>HNO₃ ₋ KNO₃ buffer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume, ml.</td>
<td>50</td>
<td>50</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Total volume, ml.</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Reaction mixture density, g./ml.</td>
<td>1.023</td>
<td>1.025</td>
<td>1.022</td>
<td>1.026</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time a</th>
<th>Conc. b</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>33.9</td>
<td>17</td>
<td>34.1</td>
<td>7</td>
<td>31.9</td>
<td>9</td>
<td>36.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>28.8</td>
<td>16</td>
<td>30.3</td>
<td>15</td>
<td>27.8</td>
<td>17</td>
<td>36.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>16.2</td>
<td>52</td>
<td>6.9</td>
<td>33</td>
<td>16.7</td>
<td>50</td>
<td>33.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>5.2</td>
<td>74</td>
<td>0.7</td>
<td>54</td>
<td>5.4</td>
<td>107</td>
<td>27.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>143</td>
<td>0.6</td>
<td>112</td>
<td>0.0</td>
<td>63</td>
<td>2.9</td>
<td>171</td>
<td>20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>199</td>
<td>0.2</td>
<td></td>
<td></td>
<td>70</td>
<td>1.2</td>
<td>235</td>
<td>13.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td>0.0</td>
<td></td>
<td>308</td>
<td>7.4</td>
<td>358</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>409</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Time in minutes  
b Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
## TABLE XXI

EXPERIMENTAL DATA FOR BLANK AND n-BUTYRALDEHYDE OXIDATIONS AT pH 1

<table>
<thead>
<tr>
<th>Run no.</th>
<th>49A</th>
<th>72A</th>
<th>73B</th>
<th>74A</th>
<th>75A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic compound</td>
<td>-</td>
<td>n-Pr CHO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>n-Pr CHO</td>
<td>n-Pr CHO</td>
<td>n-Pr CHO</td>
</tr>
<tr>
<td>Temperature, °C.</td>
<td>80.5</td>
<td>$60.00 \pm 0.05$</td>
<td>$40.00 \pm 0.05$</td>
<td>$50.00 \pm 0.05$</td>
<td>$80.00 \pm 0.05$</td>
</tr>
<tr>
<td>pH</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Initial concentration</td>
<td>-</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
</tr>
<tr>
<td>Organic compound</td>
<td>-</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0090M</td>
<td>0.0100M</td>
</tr>
<tr>
<td>ClO$_2$</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0100M</td>
<td>0.0090M</td>
<td>0.0100M</td>
</tr>
<tr>
<td>HNO$_3$ = KNO$_3$ buffer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume, ml.</td>
<td>50</td>
<td>62</td>
<td>62</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>Total volume, ml.</td>
<td>200</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Reaction mixture density, g./ml.</td>
<td>1.023</td>
<td>1.024</td>
<td>1.023</td>
<td>1.022</td>
<td>1.023</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Conc.&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
<th>Time</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>44.6</td>
<td>12</td>
<td>36.7</td>
<td>20</td>
<td>44.6</td>
<td>10</td>
<td>31.5</td>
<td>10</td>
<td>34.8</td>
</tr>
<tr>
<td>17</td>
<td>45.4</td>
<td>31</td>
<td>30.4</td>
<td>39</td>
<td>42.4</td>
<td>27</td>
<td>33.7</td>
<td>28</td>
<td>27.2</td>
</tr>
<tr>
<td>73</td>
<td>44.5</td>
<td>71</td>
<td>31.2</td>
<td>61</td>
<td>43.5</td>
<td>45</td>
<td>33.4</td>
<td>49</td>
<td>24.9</td>
</tr>
<tr>
<td>91</td>
<td>44.8</td>
<td>113</td>
<td>25.2</td>
<td>95</td>
<td>41.1</td>
<td>66</td>
<td>31.9</td>
<td>82</td>
<td>21.0</td>
</tr>
<tr>
<td>175</td>
<td>45.3</td>
<td>161</td>
<td>25.0</td>
<td>146</td>
<td>38.6</td>
<td>109</td>
<td>29.4</td>
<td>118</td>
<td>19.3</td>
</tr>
<tr>
<td>204</td>
<td>44.6</td>
<td>198</td>
<td>24.2</td>
<td>196</td>
<td>34.7</td>
<td>144</td>
<td>27.9</td>
<td>150</td>
<td>17.1</td>
</tr>
<tr>
<td>222</td>
<td>23.9</td>
<td>235</td>
<td>35.4</td>
<td>181</td>
<td>25.8</td>
<td>182</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>22.3</td>
<td>295</td>
<td>34.6</td>
<td>219</td>
<td>26.4</td>
<td>224</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>22.1</td>
<td>340</td>
<td>34.6</td>
<td>280</td>
<td>24.6</td>
<td>290</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>378</td>
<td>21.6</td>
<td>381</td>
<td>33.2</td>
<td>323</td>
<td>25.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>426</td>
<td>21.0</td>
<td>427</td>
<td>33.2</td>
<td>370</td>
<td>21.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>415</td>
<td>21.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

<sup>a</sup> n-Butyraldehyde

<sup>b</sup> Time in minutes

<sup>c</sup> Chlorine dioxide concentration in (milliequivalents total active chlorine)/(liter)
APPENDIX VI

CALCULATION METHODS FOR KINETICS CONSTANTS AT pH 1

The basic differential equation for zero order reactions is

\[-(dC/dt) = k\]

where \( C \) is concentration, \( t \) is time, and \( k \) is the reaction rate constant.

Upon integration,

\[-C = kt + \text{constant}\]

Therefore, concentration versus time plots for reactions exhibiting zero order mechanisms are a straight line. The slope of this line is equal to the reaction rate constant. Consequently, the rate constants reported in Table IV were calculated from rate plot slopes.

Activation energy calculations were based on the Arrhenius equation. In integrated form it can be written

\[\ln \left( \frac{k_2}{k_1} \right) = \frac{(\Delta E_a/R)}{[(T_2 - T_1)/T_2T_1]}\]

where \( k_1 \) is the reaction rate constant at absolute temperature \( T_1 \), \( \Delta E_a \) is the activation energy, and \( R \) is the gas law constant. This equation was solved for \( \Delta E_a \) for each reaction and the results reported in Table V.

The effect of temperature upon the rate of reaction is approximated by the temperature coefficient, \( k_t + 10^{(\log k_t)} \), where \( k \) is the reaction rate constant at \( t^\circ \) and \( k_t + 10 \) at \( 10^\circ \) higher (25, p. 1037). This value was also calculated for each reaction and reported in Table V.