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(Major Professor)

The molecular weight and percentage composition of low molecular weight organic compounds may be readily determined by equations given in this thesis, provided that such compounds may be completely oxidized by iodic acid. The percentage of carbon is found by absorbing the carbon dioxide, evolved during iodic acid oxidation, in a barium hydroxide solution and employing a double titration method. The oxidation equivalent in grams of sample oxidized by one gram atom of oxygen is found by titrating the excess potassium iodate from the oxidation with standard sodium thiosulfate solution. Should elements other than carbon, hydrogen, and oxygen be present, these must also be determined. The procedure employed utilizes a simple apparatus and technique, is adapted to intermittent operation, and is rapid and precise.
THE DETERMINATION OF MOLECULAR STRUCTURE BY IODIC ACID OXIDATION

by

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THE DETERMINATION OF MOLECULAR STRUCTURE
BY IODIC ACID OXIDATION

INTRODUCTION

More work pertaining to organic combustions has been described in the literature than perhaps any other single analytical procedure. The fact that so much attention has been devoted to this determination testifies to its importance. The problem of determining carbon and hydrogen has been approached in several ways (3,4, 5,6,8,11). In spite of all these developments there is still need for simpler techniques, less expensive equipment and methods by which the occasional determination can be made with some degree of ease.

A study of the means by which the above problem may be answered leads to one possibility, the wet combustion process. This would entail the measurement of "oxygen consumed" as an alternative for determination of moisture. Dichromate and iodate have been cited as excellent reagents for this purpose. Of these iodate is outstanding (2) since little, if any, decomposition (unless carried out above 200° C.) or CO formation accompanies its reduction.

A survey of the literature reveals that Strebinger (10)
was among the first to use iodate in this connection. He determined the oxygen requirement of an organic compound and from this and the known carbon and hydrogen content he calculated the per cent of oxygen in the compound. Later Stanek and Nemes (9) used this same reagent to determine not only the "oxygen consumed", but in addition the CO₂ evolved. The hydrogen content was calculated from the "oxygen consumed" plus other values made possible with complicated equations.

Williams (12) has also pointed out the importance of being able to determine the amount of oxygen required for complete combustion of organic material. He has developed this idea and in his paper on Oxidation Equivalent Analysis (13) describes a simple method for the determination of molecular structure based only on "oxygen consumed" and molecular weight data (plus the weight of sample). The success of this method, however, hinges upon a fairly accurate means of obtaining the molecular or equivalent weight of the compound in question.

It was the opinion of the author that the ideas presented by Williams could be much further utilized as a tool for the determination of molecular structure. Such an objective would only require the development of a simple procedure for the determination of CO₂ evolved from the reaction mixture. Due to the nature of the
evolved gases and vapors, (HCl, CO₂, I₂, H₂SO₄), it is apparent that a gravimetric method, such as described by Stanek and Nemes (9) for the determination of CO₂ would not be as desirable as a volumetric procedure. For this reason a modified Pettenkofer method (7) using a volumetric principle was devised.
APPARATUS

This apparatus is illustrated diagramatically in Fig. 1. The reaction vessel A (volume 20 ml.) was constructed from No. 15 standard taper and a capillary stopcock. The gas reservoir B consisted of a three-way stopcock, a 100 ml. burette and a leveling bulb. Mercury was used as the confining fluid. The reaction flask for the analysis of CO₂ was designed from 250 ml. Erlenmeyer, No. 20 standard taper and capillary stopcock.
Fig. 1

Diagram of a scientific apparatus with labeled parts:
- A
- B
- C
- Capillary tubing
- Rubber tubing
- 8 mm. tubing
- To leveling bulb

Fig. 1
PROCEDURE

The conditions for iodate oxidation are adequately described in the literature (10,9,13). The analysis as modified for measurement of carbon dioxide is very simple.

The reaction vessel is charged with 10-20 mg. of organic material* and sufficient potassium iodate to constitute approximately 100% excess and the system flushed with CO₂ free air.

Closing capillary stopcock a, the three-way stopcock b is then opened so as to permit the flow of emitted gases into the gas reservoir which is maintained at a slight vacuum by means of the leveling bulb.

The carbon dioxide flask is then charged with 10 ml. of approximately 0.25 N Ba(OH)₂, partially evacuated, and then connected to the other arm of the three-way stopcock.

Three ml. of concentrated H₂SO₄ is now introduced into the reaction vessel by means of the stopcock a. The charge is now ready for combustion.

*Samples such as hydroquinone which are rapidly oxidized in the cold by iodic acid can be successfully treated by first wetting the sample with a drop or two of 18 N sulfuric acid before introducing the concentrated acid.
By means of a phosphoric acid bath (1) the temperature of the reaction chamber is kept at approximately $190^\circ \pm 5^\circ$ C. for 20-40 minutes. The gases which are generated during this time pass through a U tube containing approximately 1 ml. of concentrated potassium iodide solution, to the gas holder. By operating stopcocks \text{b} and \text{c} the carbon dioxide is readily transferred to the reaction flask \text{C}.

At the end of the heating operation stopcock \text{a} is opened and 5 cc. of 18 N H$_2$SO$_4$ (to decrease the free air space) and sufficient air (CO$_2$ free) is flushed through the system to sweep all the CO$_2$ into the evacuated flask \text{C} which is then brought to atmospheric pressure.

**Determination of CO$_2$.**

The flask \text{C} is now removed and allowed to stand for thirty minutes. Ten ml. of water and 5 ml. of acetone (to improve end point) are then added and the excess Ba(OH)$_2$ is neutralized to the thymol blue end point. In order to give as sharp a change as possible 0.8 N HCl is added at the rate of approximately one-half drop per second. When within about 0.3 to 0.4 ml. of neutrality, 0.05 N acid is used to establish the end point. In the case of oxidation of an organic compound the 0.8 N HCl required can be sufficiently approximated for this pur-
pose so as not to introduce any complications.

To prevent the diffusion of air into the flask during titration, a rubber sheet (such as used for dental dam) was loosely fitted over the mouth of the flask. The tip of the burette was inserted through a small hole in the rubber. This arrangement kept out the air without complicating the procedure whatsoever.

Having neutralized the excess Ba(OH)₂, the BaCO₃ precipitate is then made slightly acid to methyl red with a known amount of standard acid. In order to insure removal of the last traces of CO₂, the solution is boiled for five minutes. The amount of 0.05 N acid required to neutralize the BaCO₃ can now be accurately determined by back titration to methyl red end point. From this data the amount of CO₂ evolved can be computed.

Preliminary experiments using either CO₂ evolved from Na₂CO₃ or straight Na₂CO₃ consistently gave high values for recovered CO₂. This constant deviation was found to depend on quantity of precipitate and to be due primarily to the apparent adsorption of Ba(OH)₂ by the BaCO₃. In order to avoid using a blank, the HCl acid was standardized with the CO₂ (evolved from either Na₂CO₃ or from the combustion of succinic acid) by means of the above procedure.
**Determination of Oxygen Consumed.**

The reaction vessel A is removed and the mixture transferred to a Kjeldahl flask, then diluted to approximately 100 ml. and steamed until disappearance of the iodine color. Sufficient Na₂CO₃ to neutralize about all but 1 ml. of 36 N H₂SO₄ acid is now added. The solution is then diluted to 200 ml. and titrated with 0.1 N sodium thiosulfate. This measures the excess iodate.

The amount of iodate used was found to be consistently greater than theoretical. This necessitated the use of a blank which amounted to .67 mg. per 100 mg. iodate used.
DISCUSSION AND RESULTS

The results of a number of typical runs are tabulated in Table I.

<table>
<thead>
<tr>
<th>Substance</th>
<th>% C</th>
<th>Calcd.</th>
<th>% H</th>
<th>Calcd.</th>
<th>E</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic Acid</td>
<td>40.66</td>
<td>40.68</td>
<td>5.22</td>
<td>5.12</td>
<td>16.83</td>
<td>16.88</td>
</tr>
<tr>
<td></td>
<td>40.71</td>
<td></td>
<td>5.18</td>
<td></td>
<td>16.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.67</td>
<td></td>
<td>5.55</td>
<td></td>
<td>16.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.91</td>
<td></td>
<td>5.12</td>
<td></td>
<td>16.76</td>
<td></td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>65.34</td>
<td>65.44</td>
<td>5.45</td>
<td>5.49</td>
<td>8.52</td>
<td>8.48</td>
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<tr>
<td></td>
<td>65.46</td>
<td></td>
<td>5.32</td>
<td></td>
<td>8.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>65.33</td>
<td></td>
<td>5.45</td>
<td></td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>69.02</td>
<td>68.34</td>
<td>4.96</td>
<td>4.95</td>
<td>8.13</td>
<td>8.14</td>
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<tr>
<td></td>
<td>68.84</td>
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<td>5.06</td>
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<tr>
<td></td>
<td>69.05</td>
<td></td>
<td>5.09</td>
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<td>8.06</td>
<td></td>
</tr>
<tr>
<td>Cinnamic Acid</td>
<td>72.73</td>
<td>72.96</td>
<td>5.48</td>
<td>5.44</td>
<td>7.43</td>
<td>7.41</td>
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<tr>
<td></td>
<td>72.96</td>
<td></td>
<td>5.44</td>
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<td>7.41</td>
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</tr>
<tr>
<td></td>
<td>72.88</td>
<td></td>
<td>5.40</td>
<td></td>
<td>7.42</td>
<td></td>
</tr>
<tr>
<td>Vanillin</td>
<td>63.22</td>
<td>63.15</td>
<td>5.22</td>
<td>5.30</td>
<td>8.96</td>
<td>8.95</td>
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<td></td>
<td>63.18</td>
<td></td>
<td>5.10</td>
<td></td>
<td>9.03</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>41.94</td>
<td>42.10</td>
<td>6.72</td>
<td>6.48</td>
<td>14.08</td>
<td>14.25</td>
</tr>
<tr>
<td></td>
<td>42.08</td>
<td></td>
<td>6.58</td>
<td></td>
<td>14.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>42.22</td>
<td></td>
<td>6.57</td>
<td></td>
<td>14.10</td>
<td></td>
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<tr>
<td>Acetylsalicylic Acid</td>
<td>60.07</td>
<td>60.00</td>
<td>4.54</td>
<td>4.47</td>
<td>9.97</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>60.21</td>
<td></td>
<td>4.52</td>
<td></td>
<td>9.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60.44</td>
<td></td>
<td>4.47</td>
<td></td>
<td>9.91</td>
<td></td>
</tr>
<tr>
<td>Phenyl Salicylate</td>
<td>72.82</td>
<td>72.89</td>
<td>4.83</td>
<td>4.71</td>
<td>7.62</td>
<td>7.66</td>
</tr>
<tr>
<td></td>
<td>73.08</td>
<td></td>
<td>4.72</td>
<td></td>
<td>7.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>73.94</td>
<td></td>
<td>4.65</td>
<td></td>
<td>7.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>73.04</td>
<td></td>
<td>4.80</td>
<td></td>
<td>7.49</td>
<td></td>
</tr>
</tbody>
</table>
Calculation of Hydrogen.

Having determined both the percent of carbon and the oxygen requirement of the compound, the percent of hydrogen can be readily calculated from the equations of Strebinger:

\[
\% H = \left(\frac{\% O_R + 100 - 1 \ 1/3 \% C}{8.93}\right)
\]

where \( O_R \) is the oxygen requirement in grams per hundred grams of sample. With compounds containing other elements in addition to carbon, hydrogen and oxygen, these calculations can be applied to the residue after correcting for such elements.

Determination of the Empirical Formula.

From the above data it is possible to make some very interesting calculations. By way of illustration let us take a specific case in which we will use the following designations:

\[ C_xH_yO_z = \text{formula of unknown} \]

\[ M = \text{molecular weight} \]

\[ N = \text{number of atoms of oxygen required to oxidize one molecule of compound} \]

\[ E = \text{grams oxidized by 1 gm. atom of oxygen} \]

then

\[
M = \frac{12 \times \% C}{\% C} = NE
\]
\[
\begin{align*}
NE &= \frac{12x}{\% C} \\
N &= \frac{12}{\% CE} = R \\
N &= Rx
\end{align*}
\]

Since \( N \) and \( x \) are integers, there must be one integer which multiplied by \( R \) will give the other integer. The possible integers (which fit this equation) can be rapidly ascertained with a slide rule.

Suppose that from the analysis of an unknown compound (benzoic acid) we obtain the following data:

\[ E = 8.12 \text{ (8.14 calcd.), } \% C = 69.3 \text{ (68.8 calcd.)}. \]

Calculating the value of \( R \) we obtain 2.13. This would give \( x \) and \( N \) the possible integral values listed below.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( N )</th>
<th>( M^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>14.92</td>
<td>122</td>
</tr>
<tr>
<td>8</td>
<td>15.05</td>
<td>138</td>
</tr>
<tr>
<td>15</td>
<td>32.0</td>
<td>260</td>
</tr>
</tbody>
</table>

Which value of \( x \), \( N \) and \( M \) is the correct one can be readily established by means of the Diophantine equations derived by Milne (12),

\[ y = \frac{(6N - M + 22z)/2}{2} \quad (a) \]
\[ z = \frac{(M - 6N + 2y)/22}{2} \quad (b) \]
\[ x = \frac{(M - 2N - 18z)/8}{2} \quad (c) \]

in which \( x \), \( y \), \( z \), \( N \) and \( M \) are integral values. Below are listed the values of \( y \) and \( z \) derived from equations

\( *M \) is always an even integer except in the case of odd molecules.
(a), (b), and (c).

<table>
<thead>
<tr>
<th>Value of x</th>
<th>Corresponding value of z</th>
<th>Corresponding value of y</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>2.22</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>4.23</td>
<td>10</td>
</tr>
</tbody>
</table>

It is evident that the formula can be none other than $C_7H_6O_2$.

In certain cases where molecular weight is large or where considerable error is made in the determination of either $E$ or percent carbon, several possible solutions may be obtained. Even under these rather adverse conditions it is still possible to determine the correct formula. In such cases differences in chemical behavior the determination of molecular or equivalent weights are a direct aid in determining the correct solution.

With the per cent carbon and "oxygen consumed" data it is also possible to ascertain the nature of the errors made during a determination (such as incorrect weights, wet or partially dehydrated samples, incomplete combustion) merely from the nature of carbon to oxygen ratios which are obtained.

**Other Applications.**

On many occasions it is only necessary to determine the per cent carbon to serve as a check on the purity of
a preparation. For such purposes this method is especially adaptable, particularly on the micro scale. Furthermore, certain compounds which are not completely oxidized at 200°C can be successfully treated at a higher temperature. In such cases oxygen equivalent data may be obtained by the dichromate method.

Limitations.

The only limitation to this method is the use of iodic acid as an oxidizing agent. Not all compounds are completely oxidized by this reagent at 200°C. The literature, however, reveals that a great many compounds can be successfully oxidized by iodic acid under conditions here specified.

In the case of compounds with high molecular weights, the determination of the molecular formula has the same limitations in accuracy as do the traditional combustion methods.

The question of compounds containing nitrogen, sulfur and halogens has not as yet been investigated in this laboratory. However, both Strebinger, Stanek and Nemes have successfully oxidized a number of such compounds with iodic acid. It is the opinion of the author that the presence of nitrogen, halogen, or sulfur in an organic compound which can be completely oxidized should offer
no complications to the method here described.

When one considers (1) the simple apparatus, (2) adaptability of the procedure to intermittent operation, (3) the amount of information derived from a single analysis, and (4) rapidity of analysis (less than two hours), it is evident that this method offers at least a partial solution to an important organic technique.
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