HEAT OF COMBUSTION OF 1-4 DIOXANE
WITH A SUPPLEMENTARY NOTE ON
THE COMBUSTION OF TRIOXANE

by

HORACE FREDERICK WHITE

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Chairman of Department of Chemistry and Professor of Chemistry In Charge of Major

Chairman of School Graduate Committee

Dean of Graduate School
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The author wishes to express his sincere appreciation for the many helpful suggestions and criticisms from Professor R. W. Spitzer, under whose direction the problem was undertaken, and from Professor E. C. Gilbert during the later stages of the investigation.

Also I wish to acknowledge the great help that I received from Mr. G. Humphrey, my co-worker, in the construction of the calorimeter.
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INTRODUCTION

Within the past quarter century, experimental techniques have been so perfected that minor ramifications of molecular structures are determinable. An example of the above implication is found in Spitzer's work on cyclic hydrocarbons (1,10,14). A continuation of this work has been proposed in this laboratory. The continuation consists in investigating the effect of introducing a foreign atom of slightly greater electronegativity (12) than carbon into the ring. Originally the plan was to determine the heats of combustion and vapor phase heat capacities of three six-membered rings containing oxygen and one five-membered oxygen heterocycle; as yet however, due to constructional difficulties, only one of the compounds has been burned and none of the heat capacities determined. This particular thesis has been modified to include construction and calibration of the apparatus as well as combustion of the compound.
APPARATUS AND PROCEDURE

The apparatus used in this study is that built by Humphrey and the author and described by Humphrey (7) in full detail. There were no changes in the apparatus for this work as it paralleled Humphrey's in many details.

The equipment used, shown in figures 5 & 6 and diagrammatically in figures 1, 2, & 7, consists of a Parr Illium double-valve bomb (360 ml. volume) immersed in an elliptic calorimeter (a=6 ½; b=4 ½; a=semi major; b=semi minor axis) containing 2536 g. of water and surrounded by a submarine jacket. This entire assembly is completely immersed in an isothermal water bath kept at constant temperature by use of a knife type heater and a mercury regulator, figure 3. A complete wiring diagram for the assembly is shown in figure 7.

The water of the calorimeter and bath is stirred by synchronous motors with the calorimeter stirrer running at approximately 420 rpm. Temperature differences in the calorimeter were determined on a Leeds and Northrup Mueller Type Bridge using a knife type L-N platinum resistance thermometer calibrated by the National Bureau of Standards. Time differences corresponding to the respective resistance deltas were recorded on a drum type chronograph sensitive to 0.01 minute over short intervals, 10 minutes, and for longer periods of time when the line voltage and current are constant. Sensitivity of this device was tested in the physics laboratory on a pendulum clock receiving standard electrical impulses.
Figure I: Schematic Diagram of Calorimeter System
Figure 2: Top View of Calorimeter and Bath

Figure 3: Thermoregulator

Figure 4: Design for Unsealed Ampoule
Legend for figures 1 and 2

1,2,3,4  Positions for determining bath temperature
B     Isothermal water bath
C     Calorimeter
D     Partition assuring uniform circulation of calorimetric fluid
F     Firing leads
G     Connecting tube between calorimeter and jacket for calorimeter stirrer shaft
H     Bath heater
M     Bath stirrer
P     Jacket positioners to assure centering of jacket
R     Thermoregulator
S     Calorimeter stirrer
T     Platinum resistance thermometer
W     Submarine jacket
Figure 5: Calorimetric System
Figure 6: Calorimetric Set Up
from the national bureau.

Ignition of the charge was accomplished by the improved ignition technique of Huffman and Ellis (6) using 7 1/2 cm. of #34 or #36 platinum wire with a two loop (1/16 inch diameter) coil in the center through which a bent filter paper fuse was hung over the charge. Approximately 1.28 calories of electrical energy (0.6 second pulse) initiated the fuse. Saturation of the bomb atmosphere with water vapor was insured by the introduction of slightly more than one gram of water from a constant delivery syringe, before the charge and 30 atmospheres of oxygen were admitted.

The standard "ordinary" calorimetric procedure described in Dickenson (2), White (19), or Weissberger (17) was used and needs no description here. Benzoic acid was burned as pellets and dioxane in open ampules, figure 4 (5), with an oil seal and an additional oil fuse. The heats of combustion of the oil ("Standard" White Oil #9, U.S.P.; a mineral oil) and the filter paper fuse (Whatman #42, ash-less) were determined by G. Humphrey (7) in this laboratory.

Paper  3974 ± 4  cal/gram
Oil     10984.3 ± 0.5  cal/gram

Nitric acid formed was titrated with standard NaOH to a brom-cresol-green end point. Dissolved CO₂ does not interfere with this end point.
Figure 7: Schematic Wiring Diagram for Calorimeter
See next page for legend
Legend for figure 7

S₁, S₂, S₃, S₄, S₅, S₆, S₇  Toggle switches for power sources

M₁  Motor for jacket stirrer; Cenco, 110V A.C., type SA-12  60 cycle, 1725 rpm., 1.8 amp., 1/12 H.P.

M₂  Motor for calorimeter stirrer; G.E. 110V A.C., type SKS, 50/60 cycle, 1500/1800 rpm., 1.9 amp., 1/30 H.P.

M₃  Motor for chronograph; Bodine, 115V A.C., type KYC-22, 60 cycle, 1 rpm., Torq. 120 in.oz.

L₁  Light for galvanometer, 60 w. bulb

L₂  Light for heater, red bulb, 10 W

R₁  Variable resistor, 725 ohm set at approximately 180 ohm

R₄  Variable resistor, 1 ohm set at approximately 0.5 ohm

Sh  Switch for shorting out R, knife type single pole, single throw

H₁  Heater for water jacket, Cenco 225 W knife type

S₀  Solenoid, activating chronograph pen

R₂  Resistor, 0.25 Meg.

K₁  Micro switch

K₂  Telegraph key

B₁  Battery, 2V

B₂  Battery, 6V

B₃  Battery, 8V

B₄  Battery, 6V

V  Voltmeter, 0-10 volts

A  Ammeter, 0-5 amps.
Several attempts at the combustion of Trioxane or Alpha Trioxymethylene proved unsuccessful. Its vapor pressure is so high that it cannot be weighed in the open. It was found that the material when packed into gelatine capsules could be weighed successfully to 0.01 mg. However the use of gelatine capsules reduced the size of sample so that complete combustion was not attained. Furthermore, determination of the heat of combustion utilizing the capsules would require a modification of technique since they contain sulfur. As suggested by Huffman and Ellis (6) as large a quantity of nitrogen as possible should be left in the bomb, without flushing, and no water introduced into it. Nitrogen insures complete combustion of sulfur to $\text{SO}_3$, contact process for $\text{H}_2\text{SO}_4$, and the elimination of water keeps the concentration of $\text{SO}_3$ in the condensate on the walls of the bomb the same as that on the bottom. If water is introduced, there is a difference in concentration of solute in the two places, and the high heat of dilution of sulfuric acid leads to erratic results.

Had time permitted, the use of cellophane wrappers might have been perfected to the point where the necessary precision in weighing could have been attained.
METHOD OF CALCULATION

The standard method of calculation for the "ordinary" calorimetric method developed by Dickenson (2) was followed.

The temperature of the water in the calorimeter and the size of the charge were so arranged that the calorimeter temperature would change about two and one half degrees. Initial temperature of the calorimeter was approximately two degrees below the bath temperature.

Figure 8 shows a characteristic curve of this calorimeter when a charge is burned in the bomb. Line $\overline{AKB}$ represents the fore period; $B$ is the firing point; $F$ represents $\Delta t_m$; $C$ is the highest temperature attained; and line $\overline{CND}$ is the post period. Extraneous material is added to illustrate the method of computing the cooling corrections which are simple applications of Newton's heat laws.

Correction of the observed data to standard states was accomplished by the Washburn method (16).

The observed quantities are:

$m$ mass of sample

$\Delta t$ Change in temperature of the calorimeter obtained from the $\Delta R$ by multiplication of $\Delta R$ by a suitable constant dependent upon the mean resistance (3).

$n_{HNO_3}$ number of moles of nitric acid formed

In order to obtain the heat of the bomb process from the temperature interval it is necessary to know the
Figure 8: Typical Time-Temperature Curve from Combustion Observations
effective heat capacity of the system. As this hypothetical instantaneous process of no temperature change but complete heat transfer is impossible, it is also necessary to know the effective heat capacity of the initial and final systems. If $C_p$ is the effective heat capacity of the calorimetric system and $S_I$ and $S_F$ are the effective heat capacities of the initial and final systems respectively, then

$$-\Delta U_B = \text{heat of the bomb process per mole of material burned at constant temperature}$$

$$= (C_p \Delta t - C_v) / n$$

$$C_v = S_I (t_H - t_I) - S_F (t_2 - t_H)$$

$$t_I = \text{initial temperature}$$

$$t_2 = \text{final temperature}$$

The values for $S_I$ and $S_F$ sufficiently accurate for any value of $\Delta t$ within the region of room temperature are readily calculated from formulas given in Washburn's article (16).

To obtain the heat evolved when the reaction occurs with all of the reactants and products in their standard states, $-\Delta U_R$, sometimes called the heat of combustion at constant volume, a percentage correction is applied to $\Delta U_B$

$$-\Delta U_R = -\Delta U_B \left[ (1 - \Delta U_{\text{corr}}) / n \Delta U_B \right]$$

$$\left( \% \text{ corr} \right) = 100 \Delta U_{\text{corr}} / n \Delta U_B$$

Again the reader is referred to Washburn equation 81 (16) for the more explicit formulation.
From this value, $\Delta U_R$, is calculated the heat of the reaction under constant pressure $\Delta H_R$ by means of the equation

$$\Delta H_R = \Delta U_R - \Delta nRT$$

where $\Delta n$ is the change in moles of gaseous substance during the reaction. It is this value, $\Delta H_R$, which is listed in the tables given in the modern literature as the heat of combustion.

In calibration of the calorimeter the above equations are rearranged solving for $C_p$. Benzoic acid sample #39f having a heat of combustion of 26.4234±0.0026 international kilojoules per gram mass (vacuo) (9), was used. Calibration figures are shown in Table I. The energy unit used in this thesis is the defined calorie,

1 calorie=0.0041833 international kilojoules.

A sample of the combustion calculation is most easily followed on the combustion record sheet, figure 9; however, some type of legend is probably necessary though most of the terms are self-explanatory.

Legend for figure 9: Calculation

- $dR$: Change of resistance in fore and post periods
- $dt$: Length of time causing $dR$
- $r(\text{obs})$: $dR/dt$
- $R(\text{mr})$: Average resistance causing $dR$ in fore and post periods
- $a$: 

$$a = \frac{[r(\text{obs}) \text{ initial} - r(\text{obs}) \text{ final}]}{R(\text{mr}) \text{ initial}}$$
## COMBUSTION RECORD
OREGON STATE COLLEGE

<table>
<thead>
<tr>
<th>Substance</th>
<th>Volume</th>
<th>Comb. No.</th>
<th>Obs. Weight</th>
<th>Date 8-4-49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. Xible</td>
<td>4,430.720</td>
<td>137</td>
<td>0.004.295</td>
<td>17.07</td>
</tr>
<tr>
<td>Wt. Xible</td>
<td>5,222.109</td>
<td>Revers</td>
<td>Wt. Unburned Fuel</td>
<td>1.71</td>
</tr>
<tr>
<td>Wt. Charge</td>
<td>0.069.611</td>
<td>Side</td>
<td>Wt. Carbon</td>
<td></td>
</tr>
<tr>
<td>Wt. Charge</td>
<td>0.609.214</td>
<td></td>
<td>Wt. Oil</td>
<td>996.20</td>
</tr>
<tr>
<td>Wt. System (air)</td>
<td>3335</td>
<td></td>
<td>Titration</td>
<td>7.431</td>
</tr>
<tr>
<td>Temp. H20</td>
<td>26</td>
<td>Total Excess</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O in Bomb</td>
<td>1 ml</td>
<td>Calories</td>
<td>1023.97</td>
<td></td>
</tr>
</tbody>
</table>

Bomb flushed X times at Y atm. Filled to Z atm.

| Initial Room Temp. | 25.5 | Final Room Temp. | 25.1 |
| Initial Bridge Temp. | 25.5 | Final Bridge Temp. | 26.2 |

### Calculation

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Time</th>
<th>Diff.</th>
<th>R</th>
<th>Time</th>
<th>Diff.</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
<td>Final</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-22.4</td>
<td>1,163.7</td>
<td>35.5</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.0059</td>
<td>0.0063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>92.49</td>
<td>803.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.0352</td>
<td>0.0355</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>8.18300</td>
<td>7.43307</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.04310</td>
<td>0.04356</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>0.04310</td>
<td>0.03791</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>9.9108</td>
<td>8.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>1.75257</td>
<td>390.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>2505.49</td>
<td>Mass (cor)</td>
<td>609.214</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>49170.5</td>
<td>Cal/gm.</td>
<td>640.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>1023.97</td>
<td>Cal Excess</td>
<td>2826086</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Remarks:
Piping Voltage = 6.05V

**Figure 9: Sample**

**Combustion Record**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15-46</td>
<td>8.1695</td>
<td>4</td>
</tr>
<tr>
<td>16-25.1</td>
<td>0.21</td>
<td>44.43.6</td>
</tr>
</tbody>
</table>
adR/2 (indicated products obvious)

\[ r(\text{corr}) \]
\[ r(\text{obs}) \text{ initial} - \text{adR/2}; r(\text{obs}) \text{ final} - \text{adR/2} \]

t(run) time of firing; and time of highest temperature

t(m) time of 0.63 total temperature change

\[ \Delta t \]
\[ t(\text{run}) - t(\text{m}) \]

\[ r\Delta t \]
\[ r(\text{corr}) \Delta t \]

R(\text{obs}) Resistance at time of firing; and at time of highest temperature

\[ R(\text{corr}) \]
\[ R(\text{obs}) - r\Delta t \]

\[ \Delta R \]
\[ R(\text{corr}) \text{ final} - R(\text{corr}) \text{ initial} \]

K Constant for changing resistance deltas to temperature deltas

\[ \Delta T \]
\[ K\Delta R \]

\[ C_p \]
Effective heat capacity of Calorimetric system

\[ C_p \Delta T \]
(indicated products obvious)

Cal Excess From total Excess Calories above. Sum of the calories involved from the combustion of the fuse and oil, the formation of HNO₃ from N₂, and the electrical energy.

\[ C_v \]
See page 14

Cal,Net \[ C_p \Delta T - \text{Cal. Excess} - C_v \]

Mass(\text{corr}) Weight of the material correct to vacuum

Cal/gram (indicated quotient obvious)

\[ R \]
Mean resistance of R(\text{corr}) for determination of K.
Dioxane: This compound was purified by the method outlined in Weissberger and Proskauer (18). 1000 g of Eastman "white label" 1-4 dioxane was refluxed for 7 hrs. with 100g (10%) of 1N HCl; a slow stream of air was passed in through the condenser to remove the aldehydes formed.

The material was then neutralized with KOH, and the aqueous layer was removed. After removing this layer, containing a brown residue - supposedly peroxides or aldehydes- the material was allowed to stand for about 2 days over KOH pellets, and then was transferred to a 2 liter distillation flask.

The dioxane was permitted to stand over Na wire for quite some time before it was distilled from the Na through a 30 plate distillation column. This distillation was done in a nitrogen atmosphere, and a reflux ratio of approximately 30/1 was maintained during the 50 hr. distillation period.

Four fractions; one 50 ml.; two 200 ml.; balance; were taken, and the center two were retained. Both fractions were stored in ground glass bottles out of the light in a nitrogen atmosphere.

The first fraction was then dried over Mg(ClO₄)₂ with a CaCl₂ tube drying all air that entered the flask. When material was needed for combustions, it was decanted with no resulting turbidity in the sample dishes.
Cryohydric analysis by the method of Mair, Glasgow, and Rossini (11) indicated that the material was 99.81 ± 0.02 mole percent pure, with a melting point of 11.6°C. No attempt at further purification was made.

Combustion data are given in Table II. Runs which were obviously incorrect due to visible carbon residues, etc., are not included in the table.

Trioxane: Dupont trioxane was dried over Mg(ClO₄)₂ for three days, and recrystallized from petroleum ether.
Table I

Water Equivalent of the Calorimeter

<table>
<thead>
<tr>
<th>N.R.S. Benzoic acid #39f wt. in vacuo, gm.</th>
<th>Corrected temperature rise °C</th>
<th>$C_p \Delta t$ (calc)</th>
<th>Heat from EIT + fuse cal.</th>
<th>Heat from HNO$_3$ cal.</th>
<th>Energy equivalent from cal./degree mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.089227</td>
<td>2.463295</td>
<td>6911.11</td>
<td>39.32</td>
<td>0.63</td>
<td>2305.63 + 0.06</td>
</tr>
<tr>
<td>1.070989</td>
<td>2.417433</td>
<td>6781.06</td>
<td>24.84</td>
<td>0.65</td>
<td>2305.06 - 0.63</td>
</tr>
<tr>
<td>1.087016</td>
<td>2.452105</td>
<td>6880.71</td>
<td>23.22</td>
<td>0.67</td>
<td>2306.04 + 0.35</td>
</tr>
<tr>
<td>1.086963</td>
<td>2.450691</td>
<td>6376.73</td>
<td>19.60</td>
<td>0.69</td>
<td>2306.05 + 0.36</td>
</tr>
</tbody>
</table>

Mean $C_p$ 2305.69

Relative mean deviation ± 0.35

Maximum deviation from the mean - 0.63
Table II
Combustion Data for 1,4-Dioxane

<table>
<thead>
<tr>
<th>Wt. Dioxane</th>
<th>Wt. Oil</th>
<th>Δt</th>
<th>$C_p Δt$</th>
<th>$C_v$</th>
<th>Cal Excess</th>
<th>Cal/gm. Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacuo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.609214</td>
<td>0.090693</td>
<td>1.75</td>
<td>4917.05</td>
<td>3.24</td>
<td>1023.97</td>
<td>6403.86 + 0.73</td>
</tr>
<tr>
<td>1.258488</td>
<td>0.099637</td>
<td>3.26</td>
<td>9162.59</td>
<td>15.92</td>
<td>1123.60</td>
<td>6400.54 - 2.59</td>
</tr>
<tr>
<td>1.290907</td>
<td>0.075453</td>
<td>3.25</td>
<td>9110.82</td>
<td>15.92</td>
<td>958.84</td>
<td>6404.72 + 1.59</td>
</tr>
<tr>
<td>1.605242</td>
<td>0.062304</td>
<td>3.96</td>
<td>11128.08</td>
<td>20.17</td>
<td>869.25</td>
<td>6403.39 + 0.26</td>
</tr>
</tbody>
</table>

Mean $-ΔU_p/m$:

Relative mean deviation:

- $ΔU_p/n$: 564.14 ± 0.12 kcal/mole
- $ΔU_R/n$: 563.73 ± 0.10 kcal/mole
- $ΔH_R/n$: 564.38 ± 0.13 Kcal/mole
DISCUSSION

The value reported for the heat of combustion of di-oxane differs from that reported by Roth and Meyer (13) by a factor of 0.5%. Their material froze from 0.7 to 0.3 degree centigrade lower than that reported here, and no specification of purity was given by them.

HEAT OF FORMATION

The heat of formation of the material from the elements in their standard states is calculated from the following set of equations:

\[ C_4H_8O_2(\text{l}) + 5 O_2(\text{g}) \rightarrow 4 CO_2(\text{g}) + 4 H_2O(\text{l}) \quad \Delta H_f = -564.38 \text{ Kcal} \]
\[ 4 CO_2(\text{g}) \rightarrow 4 C(\text{s, graphite}) + 4 O_2(\text{g}) \quad 4(-\Delta H_f) = 4(94.052) \text{ (17)} \]
\[ 4 H_2O(\text{l}) \rightarrow 4 H_2(\text{g}) + 2 O_2(\text{g}) \quad 4(-\Delta H_f) = 4(68.317) \]

Adding these equations gives

\[ C_4H_8O_2(\text{l}) \rightarrow 4 C(\text{s, graphite}) + 4 H_2(\text{g}) + O_2(\text{g}) \quad \Delta H_f = 85.10 \text{ Kcal} \]

by reversing this reaction, the formation reaction is obtained:

\[ 4 C(\text{s, graphite}) + 4 H_2(\text{g}) + O_2(\text{g}) \rightarrow C_4H_8O_2(\text{l}) \quad \Delta H_f^0 = -85.10 \text{ Kcal} \]

Since the entropy of formation of dioxane was determined by Jacobs and Parks (8), it is possible to determine the more important free energy of formation of the compound from the relation:

\[ \Delta F_f^0 = \Delta H_f^0 - T \Delta S_{298} \]
\[ \Delta S_{298} = -132.4 \text{ eu} \]
\[ T \Delta S_{298} = -39.48 \text{ Kcal} \]
\[ \Delta F_f^0 = \Delta H_f^0 - T \Delta S_{298} = -45.62 \text{ Kcal/mole} \]
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