The uncatalyzed oxidation of toluene by sulphur dioxide.

Waseem Akhtar

University of Windsor

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THE UNCATALYZED OXIDATION
OF TOLUENE BY SULFUR DIOXIDE

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
University of Windsor

by
Waseem Akhtar

Windsor, Ontario
May, 1972
To My Parents,
Sofia Bhabi and Raza

"My Lord, grant me more knowledge"
(Quran)
ABSTRACT

The oxidation of Toluene by Sulfur Dioxide was studied kinetically in the absence of a Catalyst and a Solvent. Under an initial pressure of 300 atm. and a temperature ranging from 270 to 300°C, Toluene was successfully oxidized to the corresponding carboxylic acid, i.e., Benzoic Acid. The rate of the reaction was found to be independent of Sulfur Dioxide concentration but with respect to Toluene, it could be expressed as:

\[- \frac{dC_T}{dt} = 1.10 \times 10^{20} e^{\frac{-47.59}{RT}} C_T^{1.29}\]

The Activation energy of the oxidation reaction was found to be 47.59 K. cal/mole.
ACKNOWLEDGEMENTS

The author wishes to take this opportunity to express his gratitude to Dr. G. P. Mathur for his able guidance, constructive criticism and encouragement throughout this work and to Dr. R. A. Stager and Dr. M. Adelman for their valuable suggestions on numerous occasions.

The author is also grateful to Mr. Ernie Mellonby and Mr. Dan Candido for their valuable suggestions from time to time and to Mr. G. Ryan for his technical assistance.

The financial support for the work was provided by the National Research Council of Canada.
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I. INTRODUCTION

The oxidation of hydrocarbons to the corresponding carboxylic acids by Chemical Oxidizing Agents has been under a detailed study for a long time. The most important Chemical Oxidizing agents reported to be used, so far, were: Potassium Permanganate, Dichromate in the presence of Sulfuric Acid, Hydrogen Peroxide, Ozone, Peracetic Acid, Nitric Acid, Sulfur with water and other Sulfur compounds including Sulfur Dioxide. The last two agents, i.e., Nitric Acid and Sulfur with water, have proven to be industrially successful.

The use of Sulfur Dioxide as an oxidizing agent has been a centre of interest since the late fifties. It has been tried alone, or in combination with other Sulfur compounds such as Hydrogen Sulfide, Alkali or Ammonium Sulfite.

Recently it was reported by Shipman [5] that the hydrocarbons could be oxidized successfully to the corresponding Carboxylic acids by Sulfur Dioxide under a high pressure and elevated temperatures in the absence of a Catalyst and a solvent. Since his work was primarily explorative in nature, an attempt was made here to study the kinetic aspects of the oxidation of one of the hydrocarbons by Sulfur Dioxide. Toluene was chosen, for this purpose, as the main reactant to be oxidized under an initial pressure of 300 atm. and in the temperature range of 270-300°C.
II. LITERATURE SURVEY

History of the oxidation of organic compounds by Sulfur Compounds goes back to 1887 when Willgerodt [13] reported the conversion of Aryl Methyl Ketones to Aryl Acetamides by aqueous Ammonium Polysulfide at the temperature ranging from 200-300°C.

\[
\text{C}_6\text{H}_5\text{COCH}_3 \xrightarrow{\text{Aqueous} (\text{NH}_4)_2\text{Sx}} 200-300^\circ\text{C} \xrightarrow{} \text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2
\]

Carmack and Spielman [1], in 1946, studied the same reaction in detail and reported that the aromatic hydrocarbons could not be oxidized by the Willgerodt reaction.

Later, in the early fifties, Toland [8-10] reported oxidation of hydrocarbons to their corresponding carboxylic acids by a wide variety of Sulfur Compounds in aqueous solution including elemental Sulfur in water either alone or with a base. He also studied oxidation reactions by Sulfur Dioxide alone or in combination with other Sulfur compounds such as Hydrogen Sulfide, Ammonium Sulfite and Akali Sulfide, Sulfite and Sulfate [11, 12].

Strickland and Bell [7] found that the oxidation of hydrocarbons could take place by Sulfur Dioxide over Vanadium Pentoxide catalysts at atmospheric pressure. They reported that the Sulfur Dioxide could be used as the sole source of Oxygen and as a catalyst moderator without poisoning the catalyst.
On the other hand, Shipman [5] reported that the hydrocarbon could be oxidized to corresponding carboxylic acid by Sulfur Dioxide in the absence of a catalyst and a solvent under a high pressure and elevated temperature. He studied the reaction of Sulfur Dioxide with a wide range of organic compounds particularly Toluene, Xylenes and Pseudocumene.

Shipman found that the convenient temperature and pressure ranges for the oxidation of Toluene were respectively $275^\circ$-300$^\circ$C, and 275-325 atmosphere. While for Xylene the conditions were respectively $275^\circ$-300$^\circ$C and 100-200 atmospheres. He reported that in the presence of excess Sulfur Dioxide 80-90% yields of carboxylic acids might be achieved. According to him [6] the overall oxidation reaction might be represented by the equation

$$RCH_3 + \frac{1}{2}SO_2 \rightarrow RCOOH + \frac{1}{2}S + H_2O$$

The reaction was reported to be catalyzed by compounds of Bromine and Iodine and inhibited by metallic Copper and Silver [6].
III. EXPERIMENTAL PROCEDURE

A. STRATEGY:

The objective of the present investigation was to establish the kinetics of the oxidation of Toluene by Sulfur Dioxide. On the basis of the information available in Shipman's paper [6], the oxidation reaction was studied in the temperature range of 270 to 300°C and under an initial pressure of 300 atm. It is assumed that the rate of disappearance of Toluene during the oxidation reaction can be represented by Power law expression,

\[ \frac{dC_T}{dt} = k C_T^A C_S^B \quad \text{--- (1)} \]

Where \( C_T \) is the concentration of Toluene (Mole/litre) at any time \( t \).

\( C_S \) is the concentration of \( \text{SO}_2 \) (Mole/litre) at any time \( t \).

\( A \) is the order of the reaction with respect to Toluene concentration.

\( B \) is the order of the reaction with respect to \( \text{SO}_2 \) concentration and \( k \) is the reaction velocity constant \( ((\text{Time})^{-1} (\text{Concentration}^{-A-B})) \).

In order to evaluate the parameters \( A, B \) and \( k \), two types of experimental runs were made at temperature of 285°C and under a pressure of 300 atm.; one type being stoichiometric runs, the other excess runs. In stoichiometric runs
the reactants, Toluene and Sulphur Dioxide were present in their stoichiometric ratios, i.e., 1:1.5. Thus for reactants Toluene and SO$_2$ at any time $C_g/C_T = 1.5$, so the equation (1) may be written as

$$-rac{dC_T}{dt} = k C_T^A (1.5) C_T^B = k (1.5)^B C_T^{A+B} \quad (2)$$

The integration of equation (2) leads to

$$C_{TO}^{1-A-B} - C_T^{1-A-B} = k (1-A-B) (1.5)^B t \quad (3)$$

Where $C_{TO}$ represents initial concentration of Toluene.

In excess runs, the reactant Sulphur Dioxide was present in excess of 95.28% of the required stoichiometric amount, i.e., the mole ratio of Toluene and Sulphur Dioxide was equal to 1:31.66. Under these situations, the equation (1) can be deleted as

$$-rac{dC_T}{dt} = k C_T^A C_{SO}^B \quad (4)$$

Where $C_{SO} = \text{Initial Concentration of Sulfur Dioxide (mole/litre)}$

Equation (4), on integration gives

$$C_{TO}^{1-A} - C_T^{1-A} = k (1-A) (C_{SO})^B t \quad (5)$$

Equations (3) and (5) were used in order to evaluate the parameters A, B and k by applying Non-Linear Least Square (GAUSSHAUS) Method [3].

In order to determine the activation energy of the reaction, another set of experimental runs was done at three different temperatures, i.e., 270°C, 285°C, and 300°C under
the same initial pressure of 300 atm. Using equation (3), other rate constant \((k)\) values at three different temperatures were calculated. The activation energy was, thus, found from Arrhenius' Law (i.e., \(k = k_0 e^{-E/RT}\)) by plotting \(\log k\) versus \(1/T\).

B. REACTION OPERATION:

The details of the autoclave utilized for the experimental runs are given in the reference [4]. There is therefore no need to discuss them here.

The experimental procedure most commonly used was to charge a known weight of Toluene and Sulphur Dioxide, assemble it and heat to the desired reaction temperature and an initial pressure of 300 atm. The pressure was allowed to fall during reaction. The reaction time was assumed to begin as soon as the temperature reached the desired reaction temperature.

In order to stop the reaction, the content of the reactor was cooled rapidly with the aid of the cooling coil and the removable heater of the reactor was also removed to enhance the cooling.

When the product was cooled, the remaining Sulphur Dioxide was vented and the reactor dismantled to remove the products for analysis.

C. PRODUCT ANALYSIS:

Two techniques were used to analyse the reaction product (A) Gravimetric Analysis and (B) Gas Chromatographic Analysis.
(A) Gravimetric Analysis:

This technique was used to separate Sulphur and Benzoic Acid from the product. A part of the yellow-brown product was dissolved in Ethyl Ether and filtered. The crude Sulphur, left as a residue on the filter paper, was washed two or three times with Ethyl Ether. The pure sulphur was then crystallized using Carbon Disulphide as a solvent.

The filtrate was extracted with 8% Sodium Bicarbonate. The alkaline extract, after acidification with Hydrochloric Acid gave crude light yellow Benzoic Acid. The crude Benzoic Acid was redissolved in Ether. A small amount of decolourizing Carbon was added to remove pale yellow impurities. The solution was then filtered and the purified Benzoic Acid was recovered after evaporating the Ether from the filtrate. Benzoic Acid was tested for its melting point and neutral equivalent weight which were 121-2°C and 122.4 respectively.

(B) Gas Chromatographic Analysis:

The reaction product was also analyzed by gas chromatography using a newly developed method [2]. This method was found to be excellent in separating the conventional components of Toluene oxidation product such as Benzaldehyde, Benzyl Alcohol, Diphenyl, Benzylbenzoate and unreacted Toluene.

In order to analyse the reaction product, a known amount of product was dissolved in Methyl Alcohol. The Sulphur was removed by filtration. The filtrate was mixed with a known amount of Methylbenzoate (internal standard).
A sample of 10 ul, from the solution so obtained, was injected into the column. The column was temperature programmed from 70 to 200°C using stepwise isothermal technique. In all but one experimental run only peaks for Toluene, Benzaldelyde, Methylbenzoate (internal standard) and Benzoic Acid were observed. A trace of Benzylbenzoate was, however, detected in one experimental run.

The peaks were identified by their retention times and the values were compared to those obtained with standard mixtures (refer appendix for complete detail of chromatographic analysis).
IV RESULTS

A. REACTION KINETICS:

A number of trial runs were made initially to free the autoclave of any possible leakage at the working temperature and the pressure. The final runs were then started. In all, eight final runs were made at various conditions. The details and results of the experimental runs are summarized in Table 1.

In order to evaluate the parameters A, B and k, the equations 3 and 4 were solved by the Non-Linear Least Squares (GAUSSHAUS) Method [3], using data from experimental runs 1, 2, 3 and 4. The values for A, B and k were found to be as:

\[ A = 1.29, \quad B = 0.000031 \quad \text{and} \quad k = 0.273 \]

Since the rate constant value of 0.273 was at the temperature of 285°C, other values at other temperatures 300 and 270°C were calculated using data from runs 5, 6. For this calculation equation 3 was used with values of A and B equal to 1.29 and zero respectively. The results are summarized in Table 2.

The values of \( \log_k \) vs. \( \frac{l}{T} \) were plotted in order to find out activation energy of the reaction. As shown in figure 1, the data was fitted to a straight line, the slope of which gave rise to the activation energy equal to 47.59 K.Cal/Mole. Using Arrhenius Law i.e. \( k = k_0 e^{-E/RT} \), the
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Toluene Conc. (g Mole/litre) N1</th>
<th>Initial SO$_2$ Conc. (g Mole/litre) N2</th>
<th>Mole Fraction of Toluene N1/N2+N2</th>
<th>Mole Ratio of SO$_2$ &amp; Toluene N2/N1</th>
<th>Final Toluene Conc. (g Mole/litre)</th>
<th>Reaction Time Hours</th>
<th>Reaction Temperature $^\circ$C</th>
<th>Reaction Pressure (Initial) Atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.144</td>
<td>6.253</td>
<td>0.398</td>
<td>1.5</td>
<td>2.158</td>
<td>1.75</td>
<td>285</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>4.145</td>
<td>6.250</td>
<td>0.398</td>
<td>1.5</td>
<td>1.970</td>
<td>2.50</td>
<td>285</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>0.330</td>
<td>10.450</td>
<td>0.030</td>
<td>31.66</td>
<td>0.226</td>
<td>4.50</td>
<td>285</td>
<td>300</td>
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<tr>
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<td>0.331</td>
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<td>0.030</td>
<td>31.66</td>
<td>0.208</td>
<td>6.50</td>
<td>285</td>
<td>300</td>
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<tr>
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<td>4.108</td>
<td>5.904</td>
<td>0.410</td>
<td>1.5</td>
<td>1.438</td>
<td>1.05</td>
<td>300</td>
<td>300</td>
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<td>6.406</td>
<td>0.396</td>
<td>1.5</td>
<td>2.189</td>
<td>5.50</td>
<td>270</td>
<td>300</td>
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<tr>
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<td>4.144</td>
<td>6.250</td>
<td>0.398</td>
<td>1.5</td>
<td>0.851</td>
<td>3.66</td>
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<td>300</td>
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<td>8</td>
<td>2.826</td>
<td>8.503</td>
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<td>3.00</td>
<td>0.652</td>
<td>5.16</td>
<td>285</td>
<td>300</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>$1/\sqrt{T}$</td>
<td>Rate Constants $k$ (g·Mole⁻¹·litre·Hour⁻¹)</td>
<td>log $k$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>270</td>
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<td>285</td>
<td>558</td>
<td>0.2730</td>
<td>-1.297</td>
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<td></td>
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<td></td>
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<tr>
<td>300</td>
<td>573</td>
<td>0.7757</td>
<td>-0.254</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

TABLE 2
RATES CONSTANTS VS TEMPERATURE
\[ \text{Slope} = -\frac{E}{R} = -23.95 \times 10^3 \]

Activation Energy = 47.59 K.cal/mole

**FIGURE 1: ARRHENIUS PLOT FOR OXIDATION OF TOLUENE**
frequency factor \( k_0 \) was calculated and was found to be on the order of \( 1.10 \times 10^{20} \) (Hour)\(^{-1}\) (g.Mole)\(^{-0.29}\) litre

B. PRESSURE BEHAVIOUR DURING REACTION:

A typical pressure-time plot of one of the runs is shown in figure 2 (Refer appendix for others).

This figure indicates that the reaction goes through three stages. The first is the Induction period where the pressure remains constant. The second, Falling pressure period, where the pressure begins to drop owing to the consumption of \( \text{SO}_2 \). The third, the last one is the 'tail' on the curve. The variance of Induction period was studied a bit in detail at different conditions. It was observed that the extent of the Induction period was dependent upon the temperature of reaction and the concentration of Toluene. These observations are illustrated in figures 3 and 4.

C. REACTION PRODUCT:

As mentioned in previous sections, the reaction products were analysed by two techniques, i.e., (1) Gravimetric (2) Gas chromatographic. The former was able to separate Sulfur and Benzoic Acid, while the latter identified and analysed quantitively the most common compounds usually present in the oxidation product of Toluene such as Benzaldehyde, Benzyl Alcohol, Bibenzyl, Diphenyl, Benzoic Acid, Benzylbenzoate and unreacted Toluene.

It was found that in all experimental runs except one (i.e., Run 2), the only compounds detected on the available gas chromatographic column, were Benzaldehyde and Benzoic
FIGURE 2: PRESSURE TIME PLOT FOR STOICHIOMETRIC RUN 7
FIGURE 3: INDUCTION PERIOD VS TEMPERATURE
FIGURE 4: INDUCTION PERIOD VS TOLUENE MOLE FRACTION
Acid. However, in run 2, a trace of Benzylbenzoate was detected. Other compounds which seemed to be present in the appreciable amount in some of the runs could not be identified. The unidentified mixture was of yellow-orange colour and melted in the range of 70 to 120°C. The melting point seemed to be suppressed because of the presence of elemental Sulfur. The elemental Sulfur was difficult to separate from the mixture. The detail of the analysis results are summarized in Table 3.

The percent yield of Benzoic Acid and selectivity of the reaction on the basis of Benzoic Acid and Benzaldehyde were calculated using following definitions.

\[
\text{Yield} \% = \frac{\text{Moles of Benzoic Acid formed}}{\text{Moles of Toluene introduced initially}} \times 100
\]

\[
\text{Selectivity} \% = \frac{\text{Moles of Benzoic Acid formed}}{\text{Moles of Toluene Consumed during reaction}} \times 100
\]

\[
\text{Selectivity} \% = \frac{\text{Moles of Benzaldehyde formed}}{\text{Moles of Toluene Consumed during reaction}} \times 100
\]

The unaccounted amount of Toluene, which was consumed in other side reactions to form unidentified compounds other than Benzoic Acid and Benzaldehyde, was also calculated as:

\[
\text{Selectivity} \% \text{ to products} = 100 - \text{Selectivity} \% \text{ on basis of Benzoic Acid and Benzaldehyde}
\]

The results are summarized in Table 4.

D. ACCURACY OF THE RESULTS:

The reaction products were analysed in duplicate. It was found that the accuracy of the analysis was in the range of ± 5% in the gravimetric technique while in the gas chrom-
## TABLE '3'

**PRODUCT ANALYSIS RESULTS**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Toluene Conc. (g.Mole/litre)</th>
<th>Amount of Toluene Consumed (g.Mole/litre)</th>
<th>Reaction Time Hours</th>
<th>Benzoic Acid Conc. (g.Mole/litre)</th>
<th>Benzaldehyde Conc. (g.Mole/litre)</th>
<th>Sulfur Conc. (g.Mole/litre)</th>
<th>Unidentified Compounds wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.144</td>
<td>1.986</td>
<td>1.75</td>
<td>0.375</td>
<td>0.250</td>
<td>0.901</td>
<td>39.30</td>
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<td>2</td>
<td>4.145</td>
<td>2.175</td>
<td>2.50</td>
<td>0.478</td>
<td>0.215</td>
<td>1.20</td>
<td>41.33</td>
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<tr>
<td>3</td>
<td>0.330</td>
<td>0.104</td>
<td>4.50</td>
<td>None</td>
<td>0.0131</td>
<td>Trace</td>
<td>25.26</td>
</tr>
<tr>
<td>4</td>
<td>0.331</td>
<td>0.123</td>
<td>6.50</td>
<td>0.00022</td>
<td>0.026</td>
<td>Trace</td>
<td>36.38</td>
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<td>4.108</td>
<td>2.670</td>
<td>1.05</td>
<td>0.714</td>
<td>0.198</td>
<td>1.60</td>
<td>33.00</td>
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<td>6</td>
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<td>0.088</td>
<td>0.158</td>
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<td>4.144</td>
<td>3.293</td>
<td>3.66</td>
<td>2.224</td>
<td>0.144</td>
<td>4.00</td>
<td>17.55</td>
</tr>
<tr>
<td>8</td>
<td>2.826</td>
<td>2.174</td>
<td>5.16</td>
<td>1.448</td>
<td>0.104</td>
<td>2.60</td>
<td>17.66</td>
</tr>
</tbody>
</table>
### TABLE '4'

**YIELD AND SELECTIVITIES**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reaction Temperature °C</th>
<th>Reaction Time Hours</th>
<th>Toluene Conversion %</th>
<th>Yield (Benzoic Acid) %</th>
<th>Selectivity (Basis Benzoic Acid) %</th>
<th>Selectivity (Basis Benzaldehyde) %</th>
<th>Selectivity to Products other than Benzoic Acid and Benzaldehyde %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>285</td>
<td>1.75</td>
<td>47.92</td>
<td>9.05</td>
<td>18.88</td>
<td>12.58</td>
<td>68.53</td>
</tr>
<tr>
<td>2</td>
<td>285</td>
<td>2.50</td>
<td>52.47</td>
<td>11.53</td>
<td>21.97</td>
<td>9.88</td>
<td>68.15</td>
</tr>
<tr>
<td>3</td>
<td>285</td>
<td>4.50</td>
<td>31.51</td>
<td>0.00</td>
<td>0.00</td>
<td>12.59</td>
<td>87.41</td>
</tr>
<tr>
<td>4</td>
<td>285</td>
<td>6.50</td>
<td>37.16</td>
<td>0.06</td>
<td>0.18</td>
<td>21.13</td>
<td>78.69</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>1.05</td>
<td>64.99</td>
<td>17.39</td>
<td>26.76</td>
<td>7.41</td>
<td>65.83</td>
</tr>
<tr>
<td>6</td>
<td>270</td>
<td>5.50</td>
<td>47.95</td>
<td>2.09</td>
<td>4.36</td>
<td>7.88</td>
<td>87.76</td>
</tr>
<tr>
<td>7</td>
<td>285</td>
<td>3.66</td>
<td>76.46</td>
<td>53.66</td>
<td>67.53</td>
<td>4.37</td>
<td>28.10</td>
</tr>
<tr>
<td>8</td>
<td>285</td>
<td>5.16</td>
<td>76.92</td>
<td>51.24</td>
<td>66.60</td>
<td>4.78</td>
<td>28.62</td>
</tr>
</tbody>
</table>
atographic it was $\pm 1.5\%$.

During the reaction the temperature could be controlled within the range of $\pm 3^0C$ or less. The desired initial pressure of the reaction could be achieved within the range of $\pm 3$ atm.
V. DISCUSSION

The uncatalyzed oxidation of Toluene with Sulfur Dioxide was studied in the temperature range of 270 to 300°C and under an initial pressure of 300 atm. It was found that the rate of disappearance of Toluene during the reaction could be expressed as:

\[ \frac{dC_T}{dt} = 1.10 \times 10^{20} e^{\frac{-47.59}{RT}} \cdot C_T^{1.29} \]

Where:
- \( 1.29 \) = Order of the reaction with respect to Toluene
- 47.59 = Activation energy of the reaction (k.Cal/Mole)
- \( C_T \) = Concentration of Toluene at any time 't' (hour)
- \( T \) = Temperature of the reaction (°K)
- \( R \) = Gas Constant (k.Cal/Mole X°K)

It was observed that the order of the reaction with respect to Sulfur Dioxide concentration was zero which confirmed the findings of Shipman [6]. However, in other parameter values there are differences from those reported by Shipman. For example, Shipman [6] reported that the order of the reaction with respect to Toluene and the activation energy was 2.0 and 44 k.Cal/Mole respectively which were, as compared to present values, higher in the former case and a bit lower in the latter.

Since the primary objective of this present work was to determine the rate equation of the reaction, no serious attempt, therefore, had been made to elucidate the underlying mechanisms of the reaction or to find the optimum conditions
for the reaction. However, some observations can be made on the basis of the present experimental data.

As discussed in the previous section, the reaction goes through three stages named as Induction period, Falling Pressure period and Tail period. In the first stage, i.e., Induction period, the pressure remains constant while in the second stage, the pressure falls rapidly owing to the consumption of SO₂. However in the last stage the pressure falls but very slowly. This period is thought to be caused by the final stages of the reaction taking place in a very viscous medium [6]. However, the reason for having the Induction period is unknown. One possibility is that some types of free radicals are formed during this period. For example, Shipman suggested the following reaction mechanism, analogous to the accepted mechanism for the oxidation of Toluene by oxygen.

Initiation:

\[ \text{RCH}_3 \rightarrow \text{RCH}_2^* + \text{H}^+ \]

Propagation:

\[ \text{RCH}_2 + \text{SO}_2 \rightarrow \text{R CH}_2\text{SO}_2^+ \]

\[ \text{RCH}_2\text{SO}_2^+ + \text{RCH}_3 \rightarrow \text{RCH}_2\text{SO}_2\text{H} + \text{RCH}_2^* \]

or \[ \text{RCH}_2\text{SO}_2^+ + \text{RCH}_3 \rightarrow \text{RCH}_2\text{SO}_2\text{CH}_2\text{R} + \text{H}^+ \]

Termination:

\[ \text{RCH}_2^* \quad \text{Non-initiating or} \]

\[ \text{RCH}_2\text{SO}_2^+ \quad \text{Propagating products} \]
Subsequent Reactions:

$$\text{RCH}_2\text{SO}_2\text{H} \rightarrow \text{RCOOH} + \text{H}_2\text{S}$$

$$\text{RCH}_2\text{SO}_2\text{CH}_2\text{R} \rightarrow 2\text{RCHO} + \text{H}_2\text{S}$$

$$\text{RCHO} + \frac{1}{4}\text{SO}_2 \rightarrow \text{RCOOH} + \frac{1}{2}\text{S}$$

If the above is accepted as a mechanism of oxidation of Toluene with \(\text{SO}_2\), then the initiation part of the reaction can be thought to occur during the induction period.

The effect of temperature and the concentration of Toluene on the Induction period was studied. It was observed that the extent of the Induction period was dependent on both. For example, the Induction period was only 15 minutes at \(300^\circ\text{C}\) as compared to two hours at \(270^\circ\text{C}\) for a given concentration of Toluene. On the other hand, it was one hour 10 mins. at 0.40 Toluene mole fraction as compared to 4.0 hours at 0.033 Toluene mole fraction for a given temperature \(285^\circ\text{C}\) (refer figures 3, 4).

With regards to the reaction product analysis, as shown in the previous section, only Benzoic Acid, Benzaldehyde, Sulfur and unreacted Toluene could be detected and quantitatively analysed. The other compounds, considered to be the result of side reactions, could not be identified, though the tests to identify Benzyl Alcohol, Bibenzyl, Diphenyl, Benzylbenzoate were made. The unidentified mixture was of a yellow-orange colour and melted in the range of 70 to 120\(^\circ\text{C}\).

The presence of Benzaldehyde in the reaction product confirmed the findings of Shipman. He suggested on the basis of the formation of Benzaldehyde that the reaction proceeded
via Aldehydic formation [6] i.e.:

\[ \text{RCH}_3 + \text{SO}_2 \rightarrow \text{RCHO} + \text{H}_2\text{O} + \text{S} \]

\[ \text{RCHO} + \frac{1}{2} \text{SO}_2 \rightarrow \text{RCOOH} + \frac{1}{2} \text{S} \]

The present results also lead to the same suggestion. A significant amount of Benzaldehyde was found along with Benzoic Acid (Refer Table 3). The amount of Benzaldehyde was high in those experimental runs (i.e., 1, 2, 5 and 6) which were stopped during the Falling pressure period while it was low in those runs (i.e., 7, 8) which were terminated during the Tail period.

The selectivity of the reaction and the corresponding yield of Benzoic Acid was found to be dependent upon the stage of the reaction where it was terminated and also the temperature of the reaction. As shown in table 4 for a given temperature the selectivity was the highest (i.e., 66.60, 67.53%) in runs 8, 7 and the lowest (i.e., zero) in run 3. It must be noted that in the former case the reaction had reached to the third stage, i.e., Tail period while, in the latter case, it was just near to the end of the first stage, i.e., Induction period. Similarly the effect of the temperature on the selectivity can be observed by comparing the runs 5, 2 and 6. These runs were stopped when the reaction was in the second stage, i.e., Falling pressure period. It was found that at 300°C, a higher reaction selectivity, as compared to those at 285°C and 270°C, was achieved within a shorter reaction time. This suggests that at low temperature the side reactions dominate the main reactions, while, on the other hand, at
higher temperature the side reactions are suppressed to a great extent.
VI. CONCLUSIONS AND RECOMMENDATIONS

The oxidation of Toluene by Sulfur Dioxide was studied, kinetically, in the absence of a catalyst and a solvent. It was found that in the temperature range of 270°C to 300°C and under an initial pressure of 300 atm., the rate of the reaction was independent of Sulfur Dioxide concentration but with respect to Toluene concentration, it could be expressed as

\[ \frac{dC_T}{dt} = 1.10 \times 10^{20} e^{\frac{-47.59}{RT}} C_T^{1.29} \]

It is hard to draw a conclusion with respect to the optimum conditions for the reaction on the basis of present experimental results. However, it is suggested that a reaction temperature of 300°C is the most suitable because of its high selectivity and low induction period.

Since the reaction was studied under an initial pressure of 300 atm. and in a limited range of temperatures (i.e., 270 to 300°C), efforts should be made to study the effects of various pressures and wider temperature range on the reaction yield and its selectivity. In addition, an effort should be made to establish a suitable analytical procedure to qualitatively and quantitatively analyse the unidentified compounds formed from the side reactions.

Moreover, if desired, the mechanism of the reaction
should be elucidated in order to broaden the knowledge of the high pressure effect on the chemical kinetics.
VII. REFERENCES


13. Willgerodt, C.; Ber. 202467, 1887.
VIII NOMENCLATURE

$C_T$ Concentration of Toluene at any time (g. Mole/litre)

$C_S$ Concentration of Sulfur Dioxide at any time (g. Mole/litre)

$k$ Rate Constant (Hour)$^{-1}$ (Concentration)$^{1-n}$

$n$ Overall order of the reaction

$A$ Order of reaction with respect to Toluene

$B$ Order of reaction with respect to $SO_2$

$C_{TO}$ Initial concentration of Toluene (g. Mole/litre)

$C_{SO}$ Initial concentration of $SO_2$ (g. Mole/litre)

$t$ Time of the reaction (Hour)

$g. \text{ Mole/litre}$ Gram mole/litre

$^0C$ Degree centigrade

$^0K$ Degree Kelvin

Atm. Atmosphere
APPENDIX 1

GAS CHROMATOGRAPHIC ANALYSIS
GAS CHROMATOGRAPHIC ANALYSIS

A. APPARATUS:

A Varian Aerograph Model-1520 was used with a Varian Aerograph Model 30 strip chart recorder. The chart speed was 20 inches/hour. A Disc Chart Integrator-Model 607 from Disc Instrument, Inc. was used to measure the peak area of components.

B. COLUMN:

A Gas Chromatographic Column was prepared by Chromatographic Specialties Ltd., Brockville, Ontario. The column was made of stainless steel, 4' X 0.1875" O.D. and packed with 20% Carbowax 20M on a support. The support was 60/80 Chromosorb W treated with Hexamethyldisilazane (HMDS).

C. CONDITIONS:

The column was temperature programmed from 70 to 200°C at a flow rate of 200 ml./min. During analysis the temperature was increased by stepwise isothermal technique, i.e., in the beginning of analysis, the temperature of the column was kept at 70°C for two minutes and then was increased to 125°C at the rate of 20°C/min. The column remained at 125°C for 24 minutes. Again the temperature was increased to 200°C at the rate of 20°C/min. and kept until the analysis was completed.
The detector cell temperature was maintained at 285°C and the current detectors at 150 ma. The injector temperature was kept at 240°C.

D. CALIBRATION AND ANALYSIS METHOD:

The column was calibrated with the mixtures of known compounds such as Toluene, Benzaldehyde, Benzyl Alcohol, Diphenyl, Benzoic Acid and Benzylbenzoate. Quantitative determinations of components were made by the internal standard method, using Methylbenzoate as an internal standard. To prepare the standards, a known amount of Methylbenzoate was added to the mixture of all the desired compounds of known concentration.

A 10 ml. sample was injected into the column for the analysis. The retention time and the peak area for each component was obtained. The peak area ratios of each component (peak area of component/peak area of Methylbenzoate) were plotted against the known concentration ratios (Wt. of component/Wt. of Methylbenzoate in the standard solution). A line of best fit for each component was determined by the Linear least squares technique. The retention times of all components and the equations of the lines of best fit for each component are tabulated in table 5. A Chromatogram of standard solution is illustrated in figure 5.

In the equation of lines the following terminology is used:

\[ Y = \frac{\text{Wt. of a particular component}}{\text{Wt. of Methyl Benzoate (internal standard)}} \]
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Average Retention Times (Mins.)</th>
<th>Temperature At Which Peaks Resolved °C</th>
<th>Calibration Equations**</th>
<th>Correlation Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1.0</td>
<td>70.0</td>
<td>$Y = 0.8772 \times X$</td>
<td>0.9976</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>6.50</td>
<td>125.0</td>
<td>$Y = 0.9230 \times X$</td>
<td>0.9990</td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>15.50</td>
<td>125.0</td>
<td>$Y = 1.0634 \times X$</td>
<td>0.9981</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>22.00</td>
<td>125.0</td>
<td>$Y = 1.2368 \times X$</td>
<td>0.9991</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>35.50</td>
<td>200.0</td>
<td>$Y = 1.2196 \times X$</td>
<td>0.9977</td>
</tr>
<tr>
<td>Benzyl Benzoate</td>
<td>42.00</td>
<td>200.0</td>
<td>$Y = 0.9707 \times X$</td>
<td>0.9989</td>
</tr>
<tr>
<td>Methylbenzoate (Internal Standard)</td>
<td>8.0</td>
<td>125.0</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

** $Y = \text{Wt. of a particular component}$  

\[ \frac{\text{Wt. of Methylbenzoate}}{\text{Peak area of Methylbenzoate}} \]  

$X = \text{Peak area of the particular component}$  

\[ \frac{\text{Peak area of Methylbenzoate}}{\text{Wt. of Methylbenzoate}} \]
\[ X = \frac{\text{Peak area of the component}}{\text{Peak area of Methyl Benzoate}} \]

The unknown sample to be analysed was injected to the column and the peak areas of the detected components to that of Methylbenzoate were estimated. The peak area ratio for the particular component was substituted to the corresponding equation to find the concentration ratio. From the concentration ratio, thus obtained, the concentration of the particular component was calculated by substituting the known concentration of Methylbenzoate. The chromatograms of some of the experimental runs (i.e., 2, 7) are illustrated in figures 13, 14.
APPENDIX II

PRESSURE-TIME PLOTS FOR THE EXPERIMENTAL RUNS
Temperature = $285 \pm 3^\circ C$
Initial Pressure = $300 \pm 3$ atm.
Toluene Conc. = $4.144 \text{ g mole litre}$
$\text{SO}_2$ Conc. = $6.254 \text{ g mole litre}$

FIGURE 6: PRESSURE-TIME PLOT FOR STOICHIOMETRIC RUN 1
Temperature = 285 ± 3°C
Initial Pressure = 300 ± 3 Atm.
Toluene Conc. = 4.144 g mole⁻¹ litre⁻¹
SO₂ Conc. = 6.254 g mole⁻¹ litre⁻¹

FIGURE 7: PRESSURE-TIME PLOT FOR STOICHIOMETRIC RUN 2
Temperature = 285 ± 3°C
Initial pressure = 300 ± 3 Atm.
Toluene Conc. = 0.330 g. mole
    litre
SO₂ Conc. = 10.45 g. mole
    litre

FIGURE 8: PRESSURE-TIME PLOT FOR EXCESS RUN 3
Temperature = 285 ± °C
Initial Pressure = 300 ± 3 Atm.
Toluene Conc. = 0.331 g. mole
          litre
SO₂ Conc. = 10.45 g. mole
           litre

FIGURE 9: PRESSURE-TIME PLOT FOR EXCESS RUN 4
Temperature = 300 ± 3°C
Starting Pressure = 300 ± 3 Atm.
Toluene Conc. = 4.108 g mole⁻¹ litre⁻¹
SO₂ Conc. = 5.909 g Mole⁻¹ litre⁻¹

FIGURE 10: PRESSURE-TIME PLOT FOR RUN 5
Temperature = 270 ± 5°C
Initial Pressure = 300 ± 3 Atm.
Toluene Conc. = 4.206 g mole/litre
SO₂ Conc. = 6.406 g mole/litre

FIGURE 11: PRESSURE-TIME PLOT FOR RUN 6
Temperature = 285 ± 3°C
Starting Pressure = 300 ± 3°C
Toluene Conc. = 2.826 g. mole⁻¹ litre⁻¹
SO₂ Conc. = 8.503 g. mole⁻¹ litre⁻¹

FIGURE 12: PRESSURE–TIME PLOT FOR RUN 8
APPENDIX III

MISCELLANEOUS
### TABLE 6

**PRESSURE CALIBRATION**

<table>
<thead>
<tr>
<th>Gauge Pressure (PSI)</th>
<th>Correct Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>950</td>
</tr>
<tr>
<td>2000</td>
<td>1975</td>
</tr>
<tr>
<td>3000</td>
<td>2975</td>
</tr>
<tr>
<td>4000</td>
<td>3975</td>
</tr>
<tr>
<td>5000</td>
<td>5025</td>
</tr>
</tbody>
</table>
# TABLE 7

**THERMOCOUPLE CALIBRATION**

<table>
<thead>
<tr>
<th>Mercury Thermometer °C</th>
<th>Thermo Couple (Chromel Alumal) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.5</td>
<td>99.2</td>
</tr>
<tr>
<td>78.3</td>
<td>78.7</td>
</tr>
<tr>
<td>65.7</td>
<td>65.8</td>
</tr>
<tr>
<td>50.4</td>
<td>49.9</td>
</tr>
<tr>
<td>35.5</td>
<td>35.1</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₆H₅ - CH₃</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>92.0</td>
</tr>
<tr>
<td>Boiling point</td>
<td>110.6°C</td>
</tr>
<tr>
<td>Density</td>
<td>0.8669 gm/c.c.</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>320.6°C</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>41.60 atm.</td>
</tr>
<tr>
<td>Critical Density</td>
<td>0.2913 gm/c.c.</td>
</tr>
</tbody>
</table>
TABLE 9

PHYSICAL PROPERTIES OF SULFUR DIOXIDE

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>SO₂</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>64.07</td>
</tr>
<tr>
<td>Melting point</td>
<td>-75.5°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>-10.0°C</td>
</tr>
<tr>
<td>Specific gravity liquid at 0°C</td>
<td>1.434</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>157.5°C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>77.8 atm.</td>
</tr>
<tr>
<td>Critical density</td>
<td>0.524 gm/c.c.</td>
</tr>
</tbody>
</table>
FIGURE 14: CHROMATOGRAM OF THE EXPERIMENTAL RUN 7.

RETENTION TIME (MINS.)

- Methanol (Solvent)
- Benzaldehyde
- Toluene
- Methylbenzoate
- Benzoic Acid
VITA AUCTORIS

1945  Born in U.P., India

1947  Migrated to Pakistan

1970  Received the Degree of Bachelor of Applied Science (Hons.) in Chemical Engineering from the University of Windsor, Windsor, Ontario.

1972  Candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada.