THE ROLE OF ALDEHYDES AS DEGENERATE BRANCHING INTERMEDIATE IN THE OXIDATION OF HYDROCARBONS

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Abstract   The thermal oxidation of propane in the temperature range 350-425°C was studied in order to elucidate the role of higher aldehydes as degenerate branching intermediates in the oxidation of hydrocarbons. In the slow combustion of propane, the high yield of propylene and methanol as the primary products, the formation of hydrogen peroxide, carbon monoxide, carbon dioxide, formaldehyde and steam as the final products and the presence of propylene radicals and acetaldehyde as the branching intermediate are confirmed. The effect of the addition of small quantities of acetaldehyde to propane/ oxygen mixtures was being monitored for the reduction and removal of the induction period and also changes in the maximum rate using mass spectrometry. It is concluded that the higher aldehydes and, in particular, acetaldehyde, are the degenerate branching agents in the combustion of hydrocarbons. An activation energy of 161 KJ mol⁻¹ was measured for propane oxidation which decreased when the reaction was initiated by acetaldehyde. The reaction kinetics as well as the mechanistic feature of the propane/oxygen mixture and the competitive oxidations of propane-acetaldehyde system have been investigated. The kinetics data obtained by the mass spectrometer have been analysed by computer programming and the results were represented by the appropriate kinetics plots.

Key Words   Combustion, Thermal Oxidation, Degenerate Branching, Organic Fuels, Ignition

INTRODUCTION

Investigation on the combustion of fuels has already shown that the oxidation of a fuel depends mainly on the molecular nature and on the operating conditions under which the fuel is oxidized. The combustion behaviour of organic fuels in the internal combustion engines is greatly correlated with their octane number.

The conversion of chemical energy to heat and to mechanical energy; or to potentially useful chemicals involves the ignition of fuel molecules to various extent under specified circumstances.

The low-ignition temperature fuels tend to be pre-ignited at all pressures along the lowest temperature boundary without the presence of any ignition source to produce aldehydes, ketones,
alcohols and peroxides. Such fuels exhibit knock in the internal combustion engines, thus with fuels combusted under these conditions, no useful thermal or mechanical energy can be obtained.

The high-ignition temperature fuels are combusted rapidly to generate high pressures which lead to the production of heat and mechanical energy. The fuels ignited at moderate temperatures are those prepared widely in the blended form and applied as motor fuels.

Knowledge of the branching chain mechanism and behaviour of the relatively stable intermediate products during the slow combustion of many organic fuels, suggests that such compounds play a degenerate branching role in the oxidation of hydrocarbons. The rates of formation and subsequent consumption of these intermediates are the main points which will be discussed in this article.

As a convenient example, the gas-phase oxidation of propane was studied mass spectrometrically in a static system. Acetaldehyde was selected as a possible intermediate product, the study of which could be expected to help elucidate the involvement of carbonyl compounds in the slow combustion of hydrocarbons.

EXPERIMENTAL

Propane and propylene gases were obtained from cylinders (99.5% pure instrument grade supplied by Air Products Ltd.). Acetaldehyde was prepared by vacuum fractionation of a 99% pure liquid (B.D.H.) and formaldehyde prepared by vacuum distillation of paraformaldehyde. Pure hydrogen was obtained from cylinders. Oxygen was obtained from cylinders (99.5% pure BOC) and oxygen-free nitrogen was obtained from cylinders. Hydrogen (99.9%), carbon monoxide (99.7% pure) and carbon dioxide (99.9% pure) gases were obtained from cylinders. Methanol and water vapour were prepared in appropriate vacuum distillation apparatus.

The sampling system was constructed from high vacuum pyrex glass tubings for operating under a pressure of $(2-4) \times 10^{-4}$ mm Hg. The reactor was made of clean pyrex glass in the form of an open hook and one end was connected to a probe with a small hole and the whole was suspended in an electric heating furnace which was heat insulated by the refractory bricks. The temperature was controlled by a thermocouple controller within $\pm 2^\circ C$ and its accuracy was occasionally checked by a potentiometer and adjustments were applied when required. The gas pressure was measured by a spiral gauge to an accuracy of $\pm 0.2$ mm Hg. The leak point of the reactor was connected to the ion source of a mass spectrometer MS10-C2 for continuous sampling of the reaction mixture.

RESULTS AND DISCUSSION

A number of runs were carried out at various temperatures, pressures and fuel/oxygen ratios to choose suitable conditions for studying the role of aldehydes and peroxides in the oxidation of propane. A mixture of 40 mm Hg C$_3$H$_8$ and 55 mm Hg O$_2$ at temperatures between 350 to 425°C was found to be the most practicable for this reaction system and for the mass spectrometer.

With a continuous sampling technique, required mass peak heights were obtained from repeated runs with the same fuel-oxygen mixture. Analysis was carried out by a subtractive method with calibration curves for individual compounds.

The mass peaks for a typical propane/oxygen mixture are shown in Figure 1. The decreasing peaks 27, 29 and 32 indicate the consumption of propane and oxygen respectively. The increasing peaks 42 and 43 are due mainly to the production of acetaldehyde. The increasing peaks 18, 28, 30, 31 and 44 show the formation of water, carbon monoxide,
formaldehyde, methanol and carbon dioxide, respectively. Some formic acid formation was monitored by mass peak 46.

Pressure-time curves obtained for the consumption of reactants and formation of products are shown in Figures 2 and 3. A mass balance was made for a typical oxidation mixture (Table 1).

Under the experimental conditions, (40 mm Hg C₃H₈, 55 mm Hg O₂ at 400°C) an induction period of about 12 minutes was observed; after which the pressure of the system began to increase first slowly and then sharply to a maximum (Figure 4). The variation of log ΔP with time is a straight line whose slope is the net-branching factor (Figure 5). The rate of the pressure change versus time plot is shown in Figure 6.

Both formaldehyde and acetaldehyde are found to reach maximum pressures and then decrease (Figure 3). Although formaldehyde undergoes some thermal decomposition and acetaldehyde is much more stable at the experimental temperature, the rate of acetaldehyde disappearance is much greater than that of formaldehyde.

The rate of propane consumption during the course of the reaction reached a maximum shortly after the attainment of maximum concentration of acetaldehyde. This can be attributed to the importance of acetaldehyde as a degenerate chain branching

<table>
<thead>
<tr>
<th>TABLE 1. Mass Balance for Propane Oxidation (Time of analysis = 100 minutes)</th>
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<tbody>
<tr>
<td><strong>Reactants</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Propane used</td>
</tr>
<tr>
<td>Oxygen used</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
<tr>
<td><strong>Products</strong></td>
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<tr>
<td>----------------</td>
</tr>
<tr>
<td>CH₃CHO</td>
</tr>
<tr>
<td>HCHO</td>
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<tr>
<td>C₂H₄</td>
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<tr>
<td>CO</td>
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<td>CO₂</td>
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<tr>
<td>H₂O</td>
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<tr>
<td>H₂</td>
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<tr>
<td><strong>Total</strong></td>
</tr>
<tr>
<td><strong>Difference</strong></td>
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<td><strong>Error %</strong></td>
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*The minor products such as CH₃OH, H₂O₂ and other carbon-hydrogen compounds have not been measured.
Figure 1. Mass peak height-time curves for slow oxidation of a mixture of 40 mm. Hg propane and 55 mm. Hg, O₂ at 400°C

Figure 2. Pressure-time curves for propane, oxygen and accumulated acetaldehyde in slow combustion of propane at 400°C. Initial C₃H₈ = 40; O₂ = 55 mm. Hg

Figure 3. Products formation in the oxidation of propane at 400°C. Initial C₃H₈ = 40; O₂ = 55 mm. Hg

Figure 4. Pressure change-time curve for the slow oxidation of propane at 400°C. Initial C₃H₈ = 40; O₂ = 55 mm. Hg
Reactions vessel: clean pyrex glass, dia. = 28.1 mm. Vol. = 171 mL

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intermediate in this oxidation system. Oxygen consumption was initially slow and then became steady. The rate-time curve and the rate-pressure rise curve are shown in Figures 7 and 8 respectively. The reaction rate increases linearly with pressure change and both increase exponentially with time and then decrease. The maximum rate of a typical reaction was attained after about 46% of the initial propane has been oxidized. The concentration of acetaldehyde also reached its maximum a short time before the maximum rate attainment. This is characteristic of degenerate branching chain mechanism (i.e. when

**Figure 5.** Variation of $\log(\Delta P)$ with time for propane oxidation at 400°C. Initial $C_3H_8 = 40$, $O_2 = 55$ mm Hg.

**Figure 6.** Variation of the rate of pressure change with time for propane oxidation at 400°C. Initial $C_3H_8 = 40$, $O_2 = 55$ mm Hg.

**Figure 7.** Variation of the rate of reaction with time for propane oxidation at 400°C. Initial reactants: $C_3H_8 = 40$, $O_2 = 55$ mm Hg.

**Figure 8.** Variation of the rate of reaction with pressure rise in the slow combustion of propane at 400°C. $d(M)/dt = 0$ then $d(W_{\text{kin}})/dt = 0$. Thus, if the concentration of intermediate could be kept constant, or increased by addition of intermediate then the reaction rate will be constant or increase.

**The Rate Equation**

Three series of experiments were carried out at 400°C using different propane, oxygen and total pressure. In
each series, the two other factors were constant.

The effects of initial propane, oxygen and total pressure were studied mass spectrometrically and the results were plotted in logarithmic forms (Figure 9). From the graphs obtained, for $C_3H_6/O_2 = (40-20)/55$ the order was found to be 1.58 with respect to propane, for $O_2/C_3H_6 = (55-20)/40$ the order was found to be 0.83 with respect to oxygen and for the mixtures of $O_2/C_3H_6 = 1.4$ the order was 1.07 with respect to total pressure. The following expression agrees with the experimental data obtained:

$$W_{\text{max}} = K[C_3H_6]^{1.58} \times [O_2]^{0.83} \times [P]^{1.07}$$

Total pressure has a great influence on the maximum rate since diffusion controlled surface reactions occur as the termination steps of the oxidation process [1].

With a typical oxidation mixture and the temperature region 350-425°C, an overall activation energy of about 161 kJ mole$^{-1}$ was obtained for propane oxidation (Figure 10). This is more than twice the activation energies of aldehyde oxidations.

A study of the thermochemical data of aldehydes and hydrocarbons indicates that: the aldehydes have a lower C-H bond dissociation energy than that of hydrocarbons. This probably results from the ease of initiation in aldehyde oxidations compared with that in hydrocarbon oxidations. The produced RCO and RCO$_2$ radicals are more reactive than radicals as the addition of a hydrocarbon to aldehyde/oxygen system retards the oxidation of aldehyde [2], while addition of a small amount of aldehyde or a free radical into hydrocarbon/oxygen mixture eliminates the induction period and accelerates the reaction.

**Accumulation of Intermediates**

During propane oxidation mass peaks 33, 34, 74, 75 and 76 were obtained in the order $H_3 > H_4 > H_5 > H_6 > H_7$. These peaks are characteristic of hydrogen peroxide (m/e = 33 and 34) and propyl peroxy radicals (m/e = 74, 75 and 76). Peaks 33 and 34 reached a maximum almost immediately before the maximum rate was attained, but peaks 74, 75 and 76 increased up to their maximum immediately after the maximum rate attainment. This indicates that hydroperoxides may play an important role in the branching steps of the oxidation processes. A possible reaction sequence is:
C₃H₄ + O₂ → C₃H₇ + HO₂ (i)
C₃H₅ + O₂ → C₃H₆O₂ (1)
C₃H₅O₂ + CH₄ → C₃H₁₀OOH + \dot{C}H₇ (2)

Products (non-branching)
C₃H₁OOH
C₃H₇\dot{O} + \dot{OH} (branching) (3)

Kirk and Knox, and Carlidge and Tipper have not confirmed the presence of this hydroperoxide [3,4]. The formation of aldehydes in propane/oxygen systems at low temperatures could then be the result of alkyl peroxy radical decomposition [4]:

C₃H₅O₂ → CH₃CHO + CH₅\dot{O} (4)
C₃H₇\dot{O} → CH₃CH₃CHO + \dot{OH} (5)
CH₅\dot{O} + CH₄ → CH₃OH + \dot{C}H₇ (6)

\[ \Delta H = -32.2 \text{ kJ} \]

At higher temperatures, however, a high yield of olefin is produced via the internal hydrogen abstraction of RO₂ radicals [5-8]:

\[ \text{CH₃CH₂CH}_2 \rightarrow \text{CH₃CH} \rightarrow \dot{\text{CH}}_2 \rightarrow \text{CH₃CH} = \text{CH}_2 + \text{HO}_2 \]
\[ \text{OO} \rightarrow \text{OOH} \] (7)

The dependence of the reaction rate upon the concentration of acetaldehyde produced is shown in Figure 11. The effect of the total pressure on the maximum concentration of produced acetaldehyde was studied using a mixture of 40 mm Hg C₃H₄ and 55 mm Hg O₂ with various amounts of nitrogen gas. The results observed indicate a direct dependence of produced acetaldehyde on the total pressure of the system. As Knox [5] has suggested and Ogorodnikov et al. [9], Cullis et al. [7] have confirmed, the oxidation of alkanes at low temperatures is related to the oxidation of conjugate olefins produced during the reaction [5,9] (Reaction 7). This leads to the formation of a large proportion of aldehydes, while only a minor amount of aldehyde is formed by homogeneous decomposition of alkyl peroxy radicals (Reactions 4 and 5).

During the experiment it was frequently found that in the oxidation of propane the yield of propylene was increased by an increase in the pressure or temperature of the system. This could favour Reaction 7 in the initial stages of the oxidation. The olefin produced reacts with HO₂ radicals giving a dihydroperoxide whose heterogeneous decomposition yields acetaldehyde and formaldehyde [8]

C₃H₆ + HO₂ → HOO\dot{C}₃H₆ (8)
HOO\dot{C}₃H₆ + O₂ → HOO\dot{C}₃H₆O₂ (9)
HOO\dot{C}₃H₆O₂ + HO₂ → HOO\dot{C}₃H₆OOH + O₂ (10)
HOO\dot{C}₃H₆OOH → CH₃CHO + HCHO + 2\dot{OH} (11)

The hydroxyl radicals abstract hydrogen from a molecule to form H₂O and \dot{C}₃H₆. By addition of small amounts of propylene (greater than the quantities of...
Figure 13. Mass peak height-time curves of propane-oxygen system at 400°C. Initial C\textsubscript{3}H\textsubscript{8} = 40 mm. Hg; CH\textsubscript{2}CHO = 7 mm. Hg.

Figure 14. The consumption of propane during the oxidation of 40 mm. Hg C\textsubscript{3}H\textsubscript{8} with 55 mm. Hg O\textsubscript{2} initiated by acetaldehyde: Δ = 3 mm. Hg and ● = 7 mm. Hg.

Acetaldehyde (Figure 16) shows an exponential relationship:

\[
P = K \cdot \exp(-K \tau)
\]

The effect of the added branching intermediate on

Figure 15. Products formation in the slow oxidation of propane at 400°C. Initiated by 7 mm. Hg acetaldehyde. Initial C\textsubscript{3}H\textsubscript{8} = 40; O\textsubscript{2} = 55 mm. Hg.

Figure 16. The effect of added acetaldehyde to propane-oxygen system on the induction period at 400°C. Initial C\textsubscript{3}H\textsubscript{8} = 40; O\textsubscript{2} = 55 mm. Hg.

The temperature coefficient was also studied. With a typical propane energy initiated by acetaldehyde, the activation energy was found to decrease in agreement with others [14] (Figure 10).

Mechanistic Feature

From the analytical data obtained by mass spectrometric studies of the formation and
disappearance of various reaction species, and also from the treatment of kinetics of propane oxidation process, the overall reaction mechanism may be proposed as follows:

\[
\begin{align*}
\text{C}_3\text{H}_8 + \text{O}_2 & \rightarrow (\text{n iso})\text{C}_2\text{H}_4 + \text{HO}_2 \quad (i) \\
n\text{C}_3\text{H}_7 & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 \quad (1) \\
\text{CH}_3 + \text{C}_3\text{H}_8 & \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 \quad (2) \\
n\text{iso C}_3\text{H}_7 & \rightarrow \text{C}_3\text{H}_6 + \ddot{\text{H}} \quad (3) \\
\dddot{\text{H}} + \text{C}_3\text{H}_7 & \rightarrow \text{H}_2 + \text{C}_2\text{H}_4 \quad (4) \\
n\text{- CH}_3\dddot{\text{H}} + \text{O}_2 & \rightarrow n\text{- C}_3\text{H}_2\text{OO}_2 \quad (5) \\
n\text{- C}_3\text{H}_2\text{OO} & \rightarrow \text{CH}_2\text{O} + \text{C}_2\text{H}_4 \dddot{\text{O}} \quad (6) \\
\text{C}_2\text{H}_5\dddot{\text{O}} & \rightarrow \text{CH}_2\text{O} + \text{CH}_3 \quad (7) \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \dddot{\text{OH}} \quad (8) \\
\dddot{\text{OH}} + \text{C}_3\text{H}_7 & \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_4 \quad (9) \\
\text{C}_2\text{H}_5\dddot{\text{O}} + \text{C}_3\text{H}_6 & \rightarrow \text{C}_2\text{H}_6\text{OH} + \text{C}_3\text{H}_7 \quad (10) \\
n\text{iso C}_3\text{H}_7 + \text{O}_2 & \rightarrow \text{iso C}_2\text{H}_2\text{OO} \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2 \quad (11) \\
n\text{iso C}_3\text{H}_2\text{OO} & \rightarrow \text{CH}_2\text{CHO} + \text{C}_2\text{H}_4 \dddot{O} \quad (12) \\
\text{CH}_2\dddot{\text{O}} + \text{C}_3\text{H}_7 & \rightarrow \text{CH}_2\text{OH} + \text{C}_2\text{H}_4 \dddot{\text{H}} \quad (13) \\
\text{CH}_2\text{CHO} + \text{O}_2 & \rightarrow \text{CH}_2\dddot{\text{CO}} + \text{HO}_2 \quad (14) \\
\text{CH}_2\dddot{\text{CO}} + \text{O}_2 & \rightarrow \text{M} \rightarrow \text{Products} + \text{R} \dddot{\text{C}} + \text{R}'' \quad (15) \\
\text{CH}_2\text{O} + \text{O}_2 & \rightarrow \text{HCO} + \text{HO}_2 \quad (16) \\
\text{HCO} + \text{O}_2 & \rightarrow \text{M} \rightarrow \text{products} + \text{R} \dddot{\text{C}} + \text{R}'' \quad (17) \\
(n\text{-iso})\text{C}_3\text{H}_2\dddot{\text{O}} + \text{C}_3\text{H}_7 & \rightarrow (n\text{-iso})\text{C}_3\text{H}_2\text{OOH} \quad (18) \\
(n\text{-iso})\text{C}_3\text{H}_2\text{OOH} & \rightarrow (n\text{-iso})\text{C}_3\text{H}_2\dddot{\text{O}} + \dddot{\text{OH}} \quad (19) \\
2\text{C}_3\text{H}_2\dddot{\text{O}} & \rightarrow \text{Products} \quad (20) \\
2\text{C}_3\text{H}_7 & \rightarrow \text{products} \quad (21) \\
\text{C}_3\text{H}_7 + 2\text{C}_3\text{H}_2\dddot{\text{O}} & \rightarrow \text{products} \quad (22)
\end{align*}
\]

Thus the rearrangement reactions are probably as follows:

\[
\begin{align*}
n\text{- C}_3\text{H}_7 + \text{O}_2 & \rightarrow \text{CH}_2\dddot{\text{O}} \rightarrow \text{CH}_2\dddot{\text{H}} \rightarrow \text{CH}_2\dddot{\text{CH}} \rightarrow \text{CH}_2\dddot{\text{CH}} \dddot{\text{CH}} \quad (i) \\
\dddot{\text{O}} - \dddot{\text{O}} & \rightarrow \text{H} - \text{O} - \text{O} - \text{H} \\
\text{iso C}_3\text{H}_7 + \text{O}_2 & \rightarrow \text{CH}_2\dddot{\text{O}} \rightarrow \text{CH}_2\dddot{\text{H}} \rightarrow \text{CH}_2\dddot{\text{CH}} \rightarrow \text{CH}_2\dddot{\text{CH}} \dddot{\text{CH}} \quad (ii) \\
\dddot{\text{O}} - \dddot{\text{O}} & \rightarrow \text{H} - \text{O} - \text{O} - \text{H}
\end{align*}
\]

At low temperatures the scission at (O-O) link gives formaldehyde, acetaldehyde or epoxide:

\[
\begin{align*}
\text{CH}_2\dddot{\text{O}} - \text{H} & \rightarrow \text{C} = \text{O} + \text{CH}_3\dddot{\text{H}} \\
\text{CH}_2\dddot{\text{H}} & \rightarrow \text{C} = \text{O} + \text{CH}_3\dddot{\text{H}} \\
\text{CH}_3\dddot{\text{H}} & \rightarrow \text{C} = \text{O} + \text{CH}_3\dddot{\text{H}}
\end{align*}
\]

At high temperatures, the isomerization is occurred by hydrogen atom transfer [15-20]

\[
\begin{align*}
n\text{- C}_3\text{H}_7 + \text{O}_2 & \rightarrow \text{CH}_2\dddot{\text{CH}} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} \\
\dddot{\text{O}} - \dddot{\text{O}} & \rightarrow \text{H} - \text{O} - \text{O} - \text{H} \\
\text{iso C}_3\text{H}_7 + \text{O}_2 & \rightarrow \text{CH}_2\dddot{\text{CH}} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} \\
\dddot{\text{O}} - \dddot{\text{O}} & \rightarrow \text{H} - \text{O} - \text{O} - \text{H}
\end{align*}
\]

These isomers give olefins and free radicals
\[ \text{O} \]

\[ \text{CH}_2\text{CH}:\text{CH}_2 \rightarrow \text{CH}=\text{CH}_2 + \text{H- C-H+OH} \]

\[ \text{H - O - O} \]

\[ \text{CH}_2\text{CH} - \text{CH}_2 \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HO}_2 \]

\[ \text{O - O - H} \]

From these reactions, the following important reactions which involve alkyl and alkylperoxy radicals are considered to examine the kinetic observations:

\[
\begin{align*}
\text{RH} + \text{O}_2 & \rightarrow \cdot \text{R} + \text{HO}_2 & (i) \\
\cdot \text{R} + \text{O}_2 & \rightarrow \cdot \text{RO}_2 & (1) \\
\cdot \text{R} + \text{O}_2 & \rightarrow \text{AB} + \text{HO}_2 & (1a) \\
\cdot \text{RO}_2 & \rightarrow \text{R}^* \text{CHO} + \cdot \text{R} \cdot \text{O} & (2) \\
\cdot \text{R} \cdot \text{O} + \text{RH} & \rightarrow \text{R}^* \text{OH} + \cdot \text{R} & (3) \\
\cdot \text{RO}_2 + \text{RH} & \rightarrow \text{ROOH} + \cdot \text{R} & (4) \\
\text{R}^* \text{CHO} + \text{O}_2 & \rightarrow \text{R}^* \text{CO} + \text{HO}_2 & (5) \\
\text{HO}_2 + \text{RH} & \rightarrow \text{H}_2\text{O}_2 + \cdot \text{R} & (6) \\
\text{ROOH} & \rightarrow \text{RO} + \cdot \text{OH} & (7) \\
\cdot \text{OH} + \text{RH} & \rightarrow \text{H}_2\text{O} + \cdot \text{R} & (8) \\
2\cdot \text{R} & \rightarrow \text{product} & (9) \\
2\cdot \text{RO}_2 & \rightarrow \text{product} & (10) \\
\cdot \text{R} + \cdot \text{RO}_2 & \rightarrow \text{product} & (11)
\end{align*}
\]

The rate of fuel consumption is derived from the above reaction steps as:

\[
\frac{d[\text{C}_3\text{H}_8]}{dt} = K_3[\text{R}^*\text{O}][\text{RH}] + K_4[\text{R}^*\text{O}_2][\text{RH}] + K_5[\text{OH}][\text{RH}]
\]

Since the reaction is accompanied by a relatively long induction period, step (i) is negligible. The rates of production of other species are as follows:

\[
\begin{align*}
d[\cdot \text{R} \cdot \text{O}] / dt &= K_3[\text{R}^*\text{O}][\text{O}_2][\text{RH}] = 0 \\
d[\text{HO}_2] / dt &= K_5[\text{R}^*\text{CHO}][\text{O}_2][\text{ROOH}][\text{RH}] = 0 \\
d[\cdot \text{OH}] / dt &= K_5[\text{ROOH}][\text{O}_2][\text{OH}][\text{RH}] = 0 \\
d[\text{R}^*\text{CHO}] / dt &= K_5[\text{R}^*\text{O}_2][\text{R}^*\text{CHO}][\text{O}_2][\text{RH}] = 0 \\
d[\text{ROOH}] / dt &= K_4[\text{R}^*\text{O}_2][\text{RH}][\text{ROOH}] = 0
\end{align*}
\]

By substitution of required concentrations from these data in the overall rate equation the following expression results:

\[
W = \frac{-d[\text{C}_3\text{H}_8]}{dt} = [\text{R}^*\text{CHO}] f(\text{O}_2, \text{RH})
\]

or

\[
W = [\text{RCHO}] \times f(\text{P}_{\text{tot}})
\]

This is similar to the rate equation

\[
W_{\text{max}} = a[M]_{\text{max}} \times (\text{P}_{\text{tot}} - b)
\]

which has been found experimentally. The intermediates M(aldehydes and peroxides) are formed by a non-branched chain reaction and accumulate in the system. They can react independently to give inert products or new active centers (if the energy of the secondary reactions are sufficient) which may initiate the primary chain leading to the formation of more intermediate.

**Competitive Oxidations**

In the slow combustion of propane the effective branching intermediate appears to be acetaldehyde. The \( \text{HO}_2, \cdot \text{RO} \) and \( \cdot \text{RO}_2 \) radicals responsible for the branching are thus generated via aldehyde oxidation. The presence of acetaldehyde in propane/oxygen system necessitates a competitive oxidation study of acetaldehyde and propane at 400°C.

At the point of maximum concentration of acetaldehyde the relative rate constants for radical attack on
both C₃H₈ and CH₃CHO molecules have been measured in a number of experiments and the results obtained are tabulated in Table 3.

The rate of hydroxyl radical attack to various hydrocarbon molecules is dependent on the strength of C-H bond for -CH₃ and -CH₂ groups [18] and the experimental conditions. The results obtained indicate that the rates of hydrogen removal from the lower aldehydes are considerably higher than that of propane. Hydrogen abstraction from the propane and acetaldehyde molecules by hydroxyl radicals involves an activation energy of about 22.1 KJ/mole and 16.7 KJ/mole respectively. The difference of these energies (i.e., 5.4 KJ/mole) would be sufficient to account for acetaldehyde removal by the attack of OH radicals 2.45 times faster than propane.

A mathematical estimation shows that the relative rate constants: $K_A / K_P = \frac{A_1}{A_2} e^{-E_A/E_P} R T$ for the same radical attack on both acetaldehyde and propane molecules lead to

$$\log K_A = \frac{E_P - E_A}{K_P} = \frac{1.3}{1.9872 \times 10^{-3} \times 673} = 0.972$$

whence $K_A / K_P = 2.64$

### Nomenclature

<table>
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<tr>
<th>M</th>
<th>Intermediate product</th>
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<tr>
<td>Wmax</td>
<td>Maximum rate</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
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<td>H</td>
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<td>m/e</td>
<td>Mass to charge ratio</td>
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### Table 3

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<th>Exp. No.</th>
<th>log $[C_3H_8]$</th>
<th>log $[CH_3CHO]$</th>
<th>$K_A / K_P$</th>
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The average $K_A / K_P = 2.45$.

### References


Mass Spectral Analysis of Reaction Kinetics Data Gas-Phase Oxidation of Propane at 400°C C₃H₈ = 40mm. Hg; O₂ = 55mm. Hg

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