ARE HO RADICALS PRODUCED IN THE REACTION OF O(\(^3\)P) WITH 1-\(\text{C}_4\text{H}_8\)?

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Menachem Luria, R. Simonaitis, and Julian Heicklen
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ABSTRACT

The reaction of \( O^\left( ^3P \right) \) with \( l-C_4H_8 \) was examined in the presence of CO which scavenges HO radicals to produce CO\(_2\). From the CO\(_2\) quantum yield, an upper limit to the efficiency of HO production in the reaction of \( O^\left( ^3P \right) \) with \( l-C_4H_8 \) was found to be 0.020 at both 298° and 473°K.
Since the classic work of Cvetanović, it has been accepted that \( \text{O}(^3\text{P}) \) reacts with olefins exclusively by addition to the double bond. Recently however, Huie et al. have examined the reaction over the temperature range 190-298°K which extended their previous work done over the temperature range 259-493°K. When the two sets of data were combined a non-linear Arrhenius plot was obtained. Huie et al. interpreted this non-linearity to two processes, addition to the double bond and abstraction of an H atom by the \( \text{O}(^3\text{P}) \) atom. From their rate coefficients, the abstraction should account for 15% of the reaction at 300°K and 39% at 500°K.

The possibility of H-atom abstraction from olefins by \( \text{O}(^3\text{P}) \) is intriguing. However in the work of Huie et al., such a reaction is not established since they only measured reactant removal rates. Therefore we have re-examined the \( \text{O}(^3\text{P}) + 1\text{-C}_4\text{H}_8 \) reaction in the presence of CO to see if HO really is formed. If it is, it would react rapidly with CO to produce \( \text{CO}_2 \).

The experimental procedure used was identical to that used previously in our laboratory to measure the rate of \( \text{O}(^3\text{P}) \) with CO. \( \text{O}(^3\text{P}) \) atoms were produced from the \( \text{Hg}(^6\text{P}_1) \) sensitized decomposition of \( \text{N}_2\text{O} \) in the presence of 1-C\(_4\)H\(_8\) and CO. The \( \text{N}_2\text{O} \) pressure was kept at least 3 times greater than the pressure of CO, to minimize quenching of \( \text{Hg}(^6\text{P}_1) \) by gases other than \( \text{N}_2\text{O} \). However this is unimportant, since the \( \text{O}(^3\text{P}) \) production rate is monitored by \( \text{N}_2 \) formation.

\[
\text{Hg}(^6\text{P}_1) + \text{N}_2\text{O} \rightarrow \text{Hg} + \text{N}_2 + \text{O}(^3\text{P})
\]

The only products measured were \( \text{CO}_2 \) and \( \text{N}_2 \); the quantum yield of \( \text{CO}_2 \)
formation, \( \Phi(\text{CO}_2) \), was taken as their ratio. The percent decomposition was kept small to minimize secondary reactions, the final \( \text{N}_2 \) pressures being \( \sim 65 \text{ mtorr}. \)

The results of the experiments are shown in Table I, where the reported value of \( \Phi(\text{CO}_2) \) is corrected for any dark thermal reaction. This was negligible at 298°K, but amounted to \( \sim 20\% \) at 473°K. It is readily apparent that \( \Phi(\text{CO}_2) \) is \(< 0.05 \) at both 298 and 473°K under all our conditions. The rate coefficient\(^5\) for the reaction of HO with CO is \( 5.6 \times 10^8 \exp(-1080/RT) \text{ M}^{-1} \text{ sec}^{-1} \). At room temperature the rate coefficient for HO reaction with \( 1\text{-C}_4\text{H}_8 \) is\(^6\) \( 2.4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \). It cannot be much higher at elevated temperatures. Therefore, under our conditions of \( [1\text{-C}_4\text{H}_8]/[\text{CO}] \sim 10^{-2} \) a significant portion of any HO radicals present would react with CO to produce \( \text{CO}_2 \). Consequently HO production cannot be important in the reaction of \( \text{O}(^3\text{P}) \) with \( 1\text{-C}_4\text{H}_8 \), even at 473°K.

The reactions of pertinence are:

\[
\begin{align*}
\text{O}(^3\text{P}) + 1\text{-C}_4\text{H}_8 & \to \text{not CO}_2 \text{ nor HO} & \text{2a} \\
& \to \text{CO}_2 + & \text{2b} \\
& \to \text{HO} + \text{C}_4\text{H}_7 & \text{2c} \\
\text{O}(^3\text{P}) + \text{CO} & \to \text{CO}_2 & \text{3} \\
\text{HO} + 1\text{-C}_4\text{H}_8 & \to \text{products} & \text{4} \\
\text{HO} + \text{CO} & \to \text{CO}_2 + \text{H} & \text{5}
\end{align*}
\]

Reaction 2a is the principal addition reaction of \( \text{O}(^3\text{P}) \) with \( 1\text{-C}_4\text{H}_8 \).

It is clear that reaction 2b cannot be a primary reaction since two \( \text{O}(^3\text{P}) \) atoms must be involved. It is included to account for all sources of \( \text{CO}_2 \) in the absence of CO. It is assumed that reaction 4 does not lead ultimately to \( \text{CO}_2 \) production. However if this assumption is incorrect, the conclusions are not markedly affected.
Since $k_3[\text{CO}] \ll k_2[1-\text{C}_4\text{H}_8]$, under all of our conditions the above reaction sequence leads to the expression

$$\phi'[\text{CO}_2]^{-1} = \frac{k_2}{k_{2c}} \left(1 + \frac{k_4[1-\text{C}_4\text{H}_8]}{k_5[\text{CO}]}ight)$$

where

$$\phi'[\text{CO}_2] = \phi[\text{CO}_2] - \frac{k_{2b}}{k_2} - \frac{k_3[\text{CO}]}{k_2[1-\text{C}_4\text{H}_8]}$$

and $k_2 \equiv k_{2a} + k_{2b} + k_{2c}$. The quantity $\phi'[\text{CO}_2]$ is that part of the CO$_2$ yield coming only from HO production. It is easily computed since $k_{2b}/k_2$ is $\phi[\text{CO}_2]$ in the absence of CO, and $k_3/k_2$ is known to be $1.4 \times 10^{-5}$ and $1.0 \times 10^{-4}$ at 298 and 473°K, respectively, under the conditions of our experiments (i.e. $[\text{N}_2\text{O}] \ll 200$ Torr).

Fig. 1 shows plots of $\phi'[\text{CO}_2]^{-1}$ vs $[1-\text{C}_4\text{H}_8]/[\text{CO}]$ at both 298 and 473°K. The data points are badly scattered. However straight line plots give intercepts of about 50 at both 298 and 473°K. The reciprocal of this value gives $k_{2c}/k_2 = 0.020$. This should be considered an upper limit since additional CO$_2$ might have been produced from reaction 4 or from other minor routes not considered here. In fact the ratio of the slopes to intercepts of the plots do not give values of $k_4/k_5$ consistent with literature values. This result, together with the scatter of the data, strongly indicate that the CO$_2$ observed results mainly from reactions other than reaction 2c.

This work shows that abstraction of H atoms in the reaction of O($^3\text{P}$) with $\text{C}_4\text{H}_8-1$ is not an important process. Perhaps the results of Huie et al.$^2$ can be attributed to two different addition processes.
ACKNOWLEDGEMENT

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REFERENCES


TABLE I

CO₂ Yields in the Reaction of O(3P) with 1-C₄H₈ in the Presence of CO

<table>
<thead>
<tr>
<th>[1-C₄H₈]/[CO]</th>
<th>[CO], Torr</th>
<th>[N₂O], Torr</th>
<th>( \phi(\text{CO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \infty )</td>
<td>0.0</td>
<td>265</td>
<td>0.005</td>
</tr>
<tr>
<td>0.055</td>
<td>22</td>
<td>82</td>
<td>0.010</td>
</tr>
<tr>
<td>0.033</td>
<td>33</td>
<td>182</td>
<td>0.016</td>
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<tr>
<td>0.032</td>
<td>40</td>
<td>128</td>
<td>0.012</td>
</tr>
<tr>
<td>0.024</td>
<td>45</td>
<td>158</td>
<td>0.016</td>
</tr>
<tr>
<td>0.020</td>
<td>50</td>
<td>175</td>
<td>0.013</td>
</tr>
<tr>
<td>0.017</td>
<td>65</td>
<td>220</td>
<td>0.020</td>
</tr>
<tr>
<td>0.015</td>
<td>67</td>
<td>223</td>
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</tr>
<tr>
<td>0.0097</td>
<td>87</td>
<td>274</td>
<td>0.018</td>
</tr>
<tr>
<td>0.0084</td>
<td>95</td>
<td>300</td>
<td>0.021</td>
</tr>
<tr>
<td>0.0084</td>
<td>107</td>
<td>340</td>
<td>0.024</td>
</tr>
</tbody>
</table>

\( T = 298^\circ \text{K}, [1-C₄H₈] \sim 1.1 \pm 0.2 \text{ Torr} \)

<table>
<thead>
<tr>
<th>[1-C₄H₈]/[CO]</th>
<th>[CO], Torr</th>
<th>[N₂O], Torr</th>
<th>( \phi(\text{CO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \infty )</td>
<td>0.0</td>
<td>216</td>
<td>0.006</td>
</tr>
<tr>
<td>0.033</td>
<td>48</td>
<td>255</td>
<td>0.033</td>
</tr>
<tr>
<td>0.017</td>
<td>115</td>
<td>337</td>
<td>0.040</td>
</tr>
<tr>
<td>0.016</td>
<td>85</td>
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<tr>
<td>0.016</td>
<td>90</td>
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<td>0.046</td>
</tr>
<tr>
<td>0.015</td>
<td>84</td>
<td>280</td>
<td>0.043</td>
</tr>
<tr>
<td>0.013</td>
<td>85</td>
<td>270</td>
<td>0.030</td>
</tr>
<tr>
<td>0.0091</td>
<td>120</td>
<td>368</td>
<td>0.041</td>
</tr>
</tbody>
</table>

\( T = 473^\circ \text{K}, [1-C₄H₈] = 1.5 \pm 0.5 \text{ Torr} \)
FIGURE CAPTION

Fig. 1 Plots of $\Phi'(\text{CO}_2)^{-1}$ vs $[1-\text{C}_4\text{H}_8]/[\text{CO}]$ at 298 and 473°K for the reaction of $\text{O}(^3\text{P})$ with $1-\text{C}_4\text{H}_8$ in the presence of CO.
The reaction of O(3P) with 1-C_4H_8 was examined in the presence of CO which scavenges HO radicals to produce CO_2. From the CO_2 quantum yield, an upper limit to the efficiency of HO production in the reaction of O(3P) with 1-C_4H_8 was found to be 0.020 at both 298° and 473°K.