ARE HO RADICALS PRODUCED IN THE REACTION OF O(3P) WITH 1-C₄H₈?

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\[ \text{O}(^3\text{P}) \text{ with } 1\text{-C}_4\text{H}_8? \]

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The reaction of $^{3}\text{P}O$ with $\text{1-C}_4\text{H}_8$ 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 $^{3}\text{P}O$ with $\text{1-C}_4\text{H}_8$ was found to be 0.020 at both 298° and 473°K.
Since the classic work of Cvetanović, it has been accepted that O(\(^3P\)) 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 O(\(^3P\)) 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 O(\(^3P\)) 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 O(\(^3P\)) + \(1-C_4H_8\) reaction in the presence of CO to see if HO really is formed. If it is, it would react rapidly with CO to produce CO\(_2\).

The experimental procedure used was identical to that used previously in our laboratory to measure the rate of O(\(^3P\)) with CO. O(\(^3P\)) atoms were produced from the Hg(6\(^3P_1\)) sensitized decomposition of N\(_2O\) in the presence of \(1-C_4H_8\) and CO. The N\(_2O\) pressure was kept at least 3 times greater than the pressure of CO, to minimize quenching of Hg(6\(^3P_1\)) by gases other than N\(_2O\). However this is unimportant, since the O(\(^3P\)) production rate is monitored by N\(_2\) formation.

\[
\text{Hg}(6^{3}P_1) + N_2O \rightarrow Hg + N_2 + O(3P)
\]

The only products measured were CO\(_2\) and N\(_2\); the quantum yield of CO\(_2\)
formation, $\Phi(CO_2)$, was taken as their ratio. The percent decomposition was kept small to minimize secondary reactions, the final $N_2$ pressures being ~65 mtorr.

The results of the experiments are shown in Table I, where the reported value of $\Phi(CO_2)$ is corrected for any dark thermal reaction. This was negligible at 298°K, but amounted to ~20% at 473°K. It is readily apparent that $\Phi(CO_2)$ is <0.05 at both 298 and 473°K under all our conditions. The rate coefficient 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-C$_4$H$_8$ is $2.4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. It cannot be much higher at elevated temperatures. Therefore, under our conditions of [1-C$_4$H$_8$]/[CO] $\approx 10^{-2}$ a significant portion of any HO radicals present would react with CO to produce CO$_2$. Consequently HO production cannot be important in the reaction of O($^3P$) with 1-C$_4$H$_8$, even at 473°K.

The reactions of pertinence are:

1. $O(^3P) + 1$-C$_4$H$_8 \rightarrow$ not CO$_2$ nor HO
   - 2a
   - 2b
   - 2c
2. $O(^3P) + CO \rightarrow CO_2$
   - 3
3. $HO + 1$-C$_4$H$_8 \rightarrow$ products
   - 4
4. $HO + CO \rightarrow CO_2 + H$
   - 5

Reaction 2a is the principal addition reaction of $O(^3P)$ with 1-C$_4$H$_8$. It is clear that reaction 2b cannot be a primary reaction since two $O(^3P)$ atoms must be involved. It is included to account for all sources of CO$_2$ in the absence of CO. It is assumed that reaction 4 does not lead ultimately to CO$_2$ production. However if this assumption is incorrect, the conclusions are not markedly affected.
Since \( k_3[CO] \ll k_2[1-C_4H_8] \), under all of our conditions the above reaction sequence leads to the expression

\[
\phi'[CO_2]^{-1} = \frac{k_2}{k_{2c}} \left( 1 + \frac{k_4[1-C_4H_8]}{k_5[CO]} \right)
\]

where

\[
\phi'[CO_2] \equiv \phi{CO_2} - k_{2b}/k_2 - k_3[CO]/k_2[1-C_4H_8]
\]

and \( k_2 \equiv k_{2a} + k_{2b} + k_{2c} \). The quantity \( \phi'[CO_2] \) is that part of the CO\textsubscript{2} yield coming only from HO production. It is easily computed since \( k_{2b}/k_2 \) is \( \phi{CO_2} \) 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. \([N_2O] \sim 200 \text{ Torr})\).\textsuperscript{4}

Fig. 1 shows plots of \( \phi'[CO_2]^{-1} \) vs \([1-C_4H_8]/[CO] \) 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\textsubscript{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 \( k_b/k_5 \) consistent with literature values. This result, together with the scatter of the data, strongly indicate that the CO\textsubscript{2} observed results mainly from reactions other than reaction 2c.

This work shows that abstraction of H atoms in the reaction of O\textsuperscript{(3P)} with C\textsubscript{4}H\textsubscript{8}-1 is not an important process. Perhaps the results of Huie et al\textsuperscript{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>φ(CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 298°K, [1-C₄H₈] ~ 1.1 ± 0.2 Torr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>∞</td>
<td>0.0</td>
<td>265</td>
<td>0.005</td>
</tr>
<tr>
<td>0.055</td>
<td>22</td>
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<tr>
<td>0.033</td>
<td>33</td>
<td>182</td>
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<tr>
<td>0.032</td>
<td>40</td>
<td>128</td>
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</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>
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<tr>
<td>0.017</td>
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<td>220</td>
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<tr>
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<td>274</td>
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</tr>
<tr>
<td>0.0084</td>
<td>95</td>
<td>300</td>
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</tr>
<tr>
<td>0.0084</td>
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<td>340</td>
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</tr>
<tr>
<td></td>
<td>T = 473°K, [1-C₄H₈] = 1.5 ± 0.5 Torr</td>
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<tr>
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<td>84</td>
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<tr>
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<tr>
<td>0.0091</td>
<td>120</td>
<td>368</td>
<td>0.041</td>
</tr>
</tbody>
</table>
Fig. 1  Plots of $\Phi'(CO_2)^{-1}$ vs $[1-C_4H_8]/[CO]$ at 298 and 473°K for the reaction of $O(^3P)$ with $1-C_4H_8$ in the presence of CO.
Are HO Radicals Produced in the Reaction of O(\(^3\)P) with 1-\(\text{C}_4\text{H}_8\)?

The reaction of O(\(^3\)P) with 1-\(\text{C}_4\text{H}_8\) 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(\(^3\)P) with 1-\(\text{C}_4\text{H}_8\) was found to be 0.020 at both 298° and 473°K.