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

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ABSTRACT

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.
Since the classic work of Cvetanović, it has been accepted that \( O(^{3}P) \) 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 \( O(^{3}P) \) 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 \( O(^{3}P) \) 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 \( O(^{3}P) + 1-C_{4}H_{8} \) reaction in the presence of CO to see if HO really is formed. If it is, it would react rapidly with CO to produce \( CO_{2} \).

The experimental procedure used was identical to that used previously in our laboratory to measure the rate of \( O(^{3}P) \) with CO. \( O(^{3}P) \) atoms were produced from the Hg(6\(^{3}P_{1}\)) sensitized decomposition of \( N_{2}O \) in the presence of \( 1-C_{4}H_{8} \) and CO. The \( N_{2}O \) pressure was kept at least 3 times greater than the pressure of CO, to minimize quenching of Hg(6\(^{3}P_{1}\)) by gases other than \( N_{2}O \). However this is unimportant, since the \( O(^{3}P) \) production rate is monitored by \( N_{2} \) formation.

\[
Hg(6^{3}P_{1}) + N_{2}O \rightarrow Hg + N_{2} + O(^{3}P)
\]

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 \( \approx 65 \) 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 \( \approx 20\% \) 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 \( 5.6 \times 10^8 \exp(-1080/RT) \) M\(^{-1}\) sec\(^{-1}\). At room temperature the rate coefficient for HO reaction with \( 1-C_4H_8 \) is \( 2.4 \times 10^{10} \) M\(^{-1}\) sec\(^{-1}\). It cannot be much higher at elevated temperatures. Therefore under our conditions of \( [1-C_4H_8]/[CO] \approx 10^{-2} \) 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 \( 1-C_4H_8 \), even at 473°K.

The reactions of pertinence are:

\[
\begin{align*}
0(3P) + 1-C_4H_8 & \rightarrow \text{not } CO_2 \text{ nor } HO \quad \text{2a} \\
& \rightarrow CO_2 + \quad \text{2b} \\
& \rightarrow HO + C_4H_7 \quad \text{2c} \\
O(3P) + CO & \rightarrow CO_2 \quad \text{3} \\
HO + 1-C_4H_8 & \rightarrow \text{products} \quad \text{4} \\
HO + CO & \rightarrow CO_2 + H \quad \text{5}
\end{align*}
\]

Reaction 2a is the principal addition reaction of \( O(3P) \) with \( 1-C_4H_8 \).

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

\[
\phi'\{CO_2\} = \phi\{CO_2\} - \frac{k_2b}{k_2} - \frac{k_3[CO]}{k_2[1-C_4H_8]}
\]

and \( k_2 = k_{2a} + k_{2b} + k_{2c} \). The quantity \( \phi'\{CO_2\} \) is that part of the CO₂ yield coming only from HO production. It is easily computed since \( \frac{k_2b}{k_2} \) is \( \phi\{CO_2\} \) in the absence of CO, and \( \frac{k_3}{k_2} \) 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. \([N_2O] < 200 \) Torr).

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 \( \frac{k_{2c}}{k_2} = 0.020 \). This should be considered an upper limit since additional CO₂ 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 CO₂ observed results mainly from reactions other than reaction 2c.

This work shows that abstraction of H atoms in the reaction of \( O(3^3P) \) with \( C_4H_8-1 \) is not an important process. Perhaps the results of Huie et al² 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>
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<td>340</td>
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T = 298°K, [1-C₄H₈] = 1.1 ± 0.2 Torr

<p>| | | | |</p>
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<td>368</td>
<td>0.041</td>
</tr>
</tbody>
</table>

T = 473°K, [1-C₄H₈] = 1.5 ±0.5 Torr
FIGURE CAPTION

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.
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