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

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ABSTRACT

The reaction of $^{3}\text{P}O$ with $\text{l-C}_4\text{H}_8$ 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 $\text{l-C}_4\text{H}_8$ 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 190-298ºK which extended their previous work done over the temperature range 259-493ºK. 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 300ºK and 39% at 500ºK.

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$_4$H$_8$ 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.

$$Hg(6^3P_1) + N_2O \rightarrow Hg + N_2 + O(^3P)$$

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 \textasciitilde65 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 \textasciitilde20% at 473°K. It is readily apparent that $\Phi(CO_2)$ is \textasciitilde0.05 at both 298 and 473°K under all our conditions. The rate coefficient\textsuperscript{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-C\textsubscript{4}H\textsubscript{8} is $6.4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. It cannot be much higher at elevated temperatures. Therefore under our conditions of $[1-C_4H_8]/[CO] \approx 10^{-2}$ a significant portion of any HO radicals present would react with CO to produce CO\textsubscript{2}. Consequently HO production cannot be important in the reaction of $O(^3P)$ with 1-C\textsubscript{4}H\textsubscript{8}, even at 473°K.

The reactions of pertinence are:

\begin{align*}
O(^3P) + 1-C_4H_8 &\to \text{not CO}_2 \text{ nor HO} & 2a \\
&\to CO_2+ & 2b \\
&\to HO + C_4H_7 & 2c \\
O(^3P) + CO &\to CO_2 & 3 \\
HO + 1-C_4H_8 &\to \text{products} & 4 \\
HO + CO &\to CO_2 + H & 5
\end{align*}

Reaction 2a is the principal addition reaction of $O(^3P)$ with 1-C\textsubscript{4}H\textsubscript{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\textsubscript{2} in the absence of CO. It is assumed that reaction 4 does not lead ultimately to CO\textsubscript{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

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

where

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

and \( k_2 \equiv k_{2a} + k_{2b} + k_{2c} \). The quantity \( \phi'[\text{CO}_2] \) is that part of the \( \text{CO}_2 \) yield coming only from \( \text{HO} \) production. It is easily computed since \( \frac{k_{2b}}{k_2} \) is \( \Phi[\text{CO}_2] \) in the absence of \( \text{CO} \), 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. \([\text{N}_2\text{O}] \lesssim 200 \text{Torr}\)).

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 \( \text{CO}_2 \) 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 \( k_h/k_5 \) consistent with literature values. This result, together with the scatter of the data, strongly indicate that the \( \text{CO}_2 \) observed results mainly from reactions other than reaction 2c.

This work shows that abstraction of \( \text{H} \) atoms in the reaction of \( \text{O}(^3\text{P}) \) 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

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T = 298°C, [1-C₄H₈] = 1.1 ± 0.2 Torr

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T = 473°C, [1-C₄H₈] = 1.5 ± 0.5 Torr
Fig. 1 Plots of $\Phi'(\text{CO}_2)^{-1}$ vs $[1-C_4H_8]/[\text{CO}]$ at 298 and 473°K for the reaction of $O(^3\text{P})$ with $1-C_4H_8$ in the presence of CO.
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