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IONOSPHERIC RESEARCH

Scientific Report 409

ARE HO RADICALS PRODUCED IN THE REACTION OF $O(^3P)$ WITH $1\text{-}C_4H_8$?

by
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ABSTRACT

The reaction of $O(^3P)$ with $1\text{-}C_4H_8$ 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 $1\text{-}C_4H_8$ was found to be 0.020 at both 298° and 473°K.

Since the classic work of Cvetanović,[1] it has been accepted that $O(^3P)$ reacts with olefins exclusively by addition to the double bond. Recently however, Huie et al.[2] have examined the reaction over the temperature range 190-298°K which extended their previous work[3] 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[2] 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,[2] 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.[4] $O(^3P)$ 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.

$$Hg(6^3P_1) + N_2O \rightarrow Hg + N_2 + O(^3P) \qquad 1$$

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 $\sim$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 $\sim$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[5] for the reaction of HO with CO is $5.6 \times 10^8 \exp(-1080/RT)$ $\underline{M}^{-1}$ sec^{-1}. At room temperature the rate coefficient for HO reaction with $1\text{-}C_4H_8$ is[6] 2.4×10^{10} $\underline{M}^{-1}$ sec^{-1}. It cannot be much higher at elevated temperatures. Therefore under our conditions of $[1\text{-}C_4H_8]/[CO] \sim 10^{-2}$ 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 $1\text{-}C_4H_8$, even at 473°K.

The reactions of pertinence are:

$O(^3P) + 1\text{-}C_4H_8$	$\rightarrow$ not CO_2 nor HO	2a
	$\rightarrow CO_2 +$	2b
	$\rightarrow HO + C_4H_7$	2c
$O(^3P) + CO$	$\rightarrow CO_2$	3
$HO + 1\text{-}C_4H_8$	$\rightarrow$ products	4
$HO + CO$	$\rightarrow CO_2 + H$	5

Reaction 2a is the principal addition reaction of $O(^3P)$ with $1\text{-}C_4H_8$. 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 $k_3[CO] << k_2[1\text{-}C_4H_8]$, under all of our conditions[4] the above reaction sequence leads to the expression

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

where

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

and $k_2 \equiv k_{2a} + k_{2b} + k_{2c}$. The quantity $\Phi'\{CO_2\}$ is that part of the CO_2 yield coming only from HO production. It is easily computed since k_{2b}/k_2 is $\Phi\{CO_2\}$ in the absence of CO, and k_3/k_2 is known to be 1.4×10^{-5} and 1.0×10^{-4} at 298 and 473°K, respectively, under the conditions of our experiments (i.e. $[N_2O] \sim 200$ Torr).[4]

Fig. 1 shows plots of $\Phi'\{CO_2\}^{-1}$ vs $[1\text{-}C_4H_8]/[CO]$ 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_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 $O(^3P)$ with C_4H_8-1 is not an important process. Perhaps the results of Huie et al[2] can be attributed to two different addition processes.

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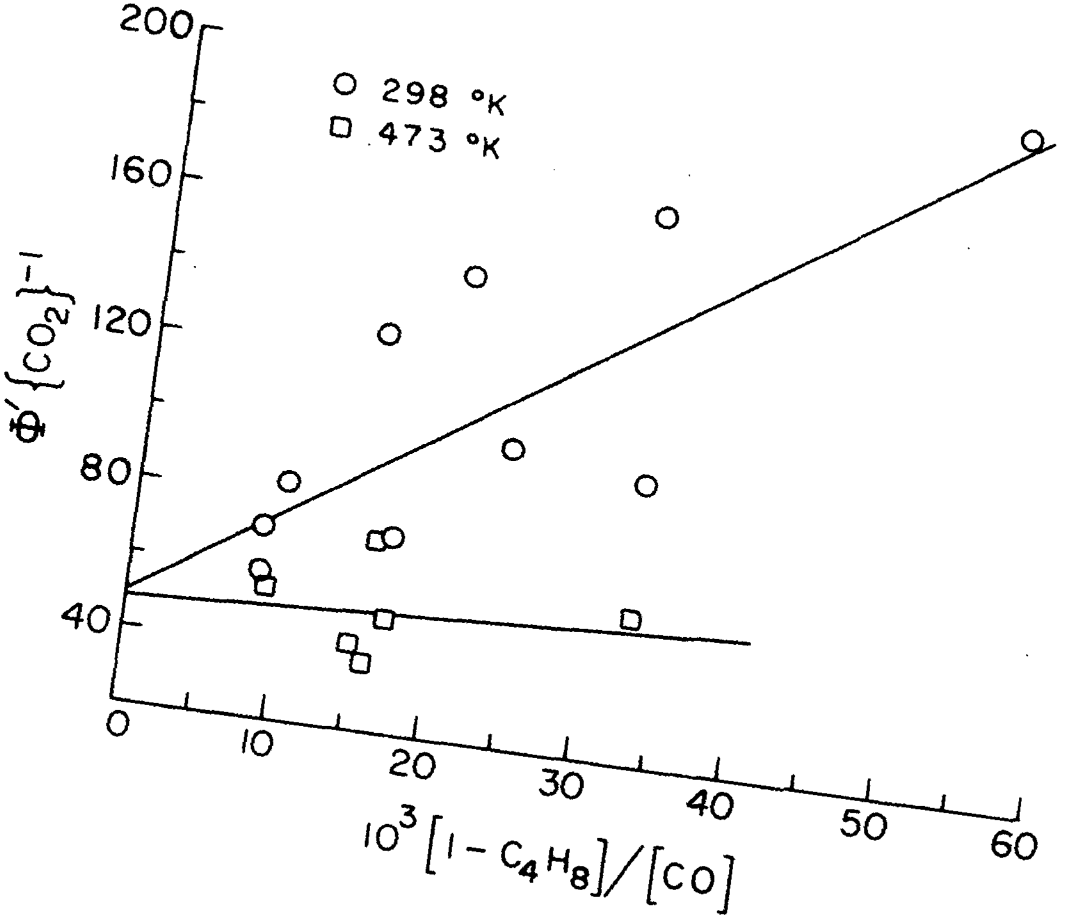
TABLE I

CO_2 Yields in the Reaction of $O(^3P)$ with $1\text{-}C_4H_8$ in the Presence of CO

$[1\text{-}C_4H_8]/[CO]$	[CO], Torr	$[N_2O]$, Torr	$\Phi\{CO\}$
	T = 298°K, $[1\text{-}C_4H_8] \sim 1.1 \pm 0.2$ Torr		
∞	0.0	265	0.005
0.055	22	82	0.010
0.033	33	182	0.016
0.032	40	128	0.012
0.024	45	158	0.016
0.020	50	175	0.013
0.017	65	220	0.020
0.015	67	223	0.014
0.0097	87	274	0.018
0.0084	95	300	0.021
0.0084	107	340	0.024
	T = 473°K, $[1\text{-}C_4H_8] = 1.5 \pm 0.5$ Torr		
∞	0.0	216	0.006
0.033	48	255	0.033
0.017	115	337	0.040
0.016	85	255	0.034
0.016	90	285	0.046
0.015	84	280	0.043
0.013	85	270	0.030
0.0091	120	368	0.041

FIGURE CAPTION

Fig. 1 Plots of $\Phi'\{CO_2\}^{-1}$ vs $[1\text{-}C_4H_8]/[CO]$ at 298 and 473°K for the reaction of $O(^3P)$ with $1\text{-}C_4H_8$ in the presence of CO.



200
160
120
80
40
0
10
20
30
40
50
60
○ 298 °K
□ 473 °K
$\Phi'\{CO_2\}^{-1}$
$10^3[1-C_4H_8]/[CO]$

Fig. 1

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