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Short Communication

Methods for OH generation in the presence of olefins: evidence for H atom abstraction from propylene by hydroxyl radicals

J. P. L. HENRI and R. W. CARR, Jr.

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455 (U.S.A.)

The importance of OH–olefin reactions in photochemical smog has been discussed in recent investigations [1, 2]. Although $OH-C_2H_4$ and $OH-C_3H_6$ adducts formed at 1 Torr have been observed mass spectrometrically [3], and other fragments of the $OH-C_3H_6$ reaction have been observed at molecular beam conditions [4], no investigation of the mechanism of OH–olefin reactions at 1 atm. has appeared yet. In this communication we evaluate three methods of OH generation in the presence of propylene by steady-illumination photolysis methods. The experiments provide indirect evidence that allyl radicals are formed at all experimental conditions used. Relative rate considerations suggest that OH can abstract H from the allyl position of propylene.

Experiments were done with a conventional vacuum apparatus (10^{-5} Torr) having Teflon glass valves with viton O rings. The cylindrical reactor (10 cm × 3.3 cm diam.) had Ultrasil end windows. The three series of experiments were: (1) 228.8 nm photolysis of $NO_2/H_2/C_3H_6$ mixtures, 1.3: 96.3: 6.4 mol %, respectively at 740 Torr and 300 °K; (2) 213.9 nm photolysis of $N_2O/H_2/C_3H_6$ mixtures, 1.7: 96.3: 2.0 mol %, respectively at 690 Torr and 300 °K; and (3) 213.9 nm photolysis of $N_2O/H_2O/C_3H_6$ mixtures, 3.3: 91.5: 5.2 mol %, respectively, at 612 Torr and 500 °K.

Reaction products were identified gas chromatographically by comparison with retention times of authentic samples on three ¼ in. o.d. columns: 3 m diisodecyl phthalate, 20 wt % on 60 - 80 mesh firebrick at 80 °C, 2.2 m β, β' - oxydipropionitrile, 20 wt % on 60 - 80 mesh Chromosorb P at both 68° and 0 °C, and 1 m silica gel at 68 °C. Table 1 gives the reaction product distributions, expressed as % of total measured products.

In series (1), reaction is initiated by NO_2 photolysis at 228.8 nm, yielding $O(^1D)$ [5]. This is followed by reactions (1) - (8), which occur to greater or lesser extent, as discussed below.
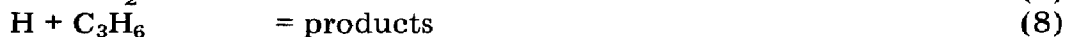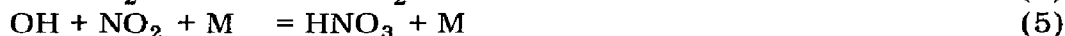
TABLE 1

Reaction product yields

Product	Relative yields[a]		
	$NO_2/H_2/C_3H_6$	$N_2O/H_2/C_3H_6$	$N_2O/H_2O/C_3H_6$
ethane		0.006	
	0.03[b]		0.38[b]
ethylene		0.11	
methanol	0.03	- - -[c]	- - -
A formaldehyde	0.11	- - -	- - -
2-methyl-2-butene	0.004	0.14	0.17
3-methyl-1-butene	- - -	0.04	0.08
1-pentene	- - -	0.05	0.04
2-methyl-1-butene	- - -	0.05	0.02
trans-2-pentene	- - -	0.05	0.26
1,5-hexadiene	0.04	0.54	0.02
ethanol	0.33	- - -	- - -
propionaldehyde	0.09	- - -	- - -
isopropanol	0.04	- - -	- - -
n-propanol	0.05	- - -	- - -
formic acid	0.06	- - -	- - -
acetic acid	0.04	- - -	- - -
B	0.04	- - -	- - -
D	0.05	- - -	- - -
E	0.05	- - -	- - -
F	0.04	- - -	- - -
I	- - -	- - -	0.04

[a]Yields expressed as fraction of total measured products.
[b]Combined C_2H_4 and C_2H_6 yield.
[c]- - - means not observed.

$$O(^1D) + H_2 \quad = OH + H \tag{1}$$
$$O(^1D) + NO_2 \quad = NO + O_2 \tag{2}$$
$$O(^1D) + C_3H_6 \quad = products \tag{3}$$
$$OH + H_2 \quad = H + H_2O \tag{4}$$
$$OH + NO_2 + M \quad = HNO_3 + M \tag{5}$$
$$OH + C_3H_6 \quad = products \tag{6}$$
$$H + NO_2 \quad = NO + OH \tag{7}$$
$$H + C_3H_6 \quad = products \tag{8}$$

In each of the three series, conversions were kept sufficiently low that reactions of H, $O(^1D)$ and OH with products was not considered important. Using recent values of k_1 [6], k_2 [6], and assuming $k_3 = 10^{-10}$ cm^3 molecule^{-1} s^{-1}, a value close to the rate constants for several other $O(^1D)$ reactions, all of which are close to the collision frequency, we calculate $R_2/R_1 = 0.012$ and $R_3/R_1 = 0.05$ for the relative rates of reactions (2) and (1), and (3) and (1). Similarly, recent values of k_4 [7], k_5 [8] and k_6 [9] yield $R_4/R_6 = 0.009$ and $R_5/R_6 = 0.1$; and values of k_7 [10] and k_8 [11] yielded $R_8/R_7 = 0.001$. Thus reactions (1), (6) and (7) are the principal mechanism for removal of $O(^1D)$, OH, and H, respectively.

In series (2), a comparable reaction mechanism is initiated by N_2O photolysis, $N_2O + h\nu(213.9 \text{ nm}) = N_2 + O(^1D)$ [12], followed by reactions (1), (3), (4), (6), (8), (9a) and (9b). With

$$O(^1D) + N_2O = N_2 + O_2 \tag{9a}$$
$$= 2NO \tag{9b}$$

$k_{9a} = k_{9b} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $R_9/R_1 = 0.014$; $R_3/R_1 = 0.015$; $R_4/R_6 = 0.03$, from which we conclude that $O(^1D)$ reacts predominantly with H_2, and OH reacts predominantly with C_3H_6.

Finally, in series (3), $O(^1D)$ from N_2O photolysis at 213.9 nm produces OH by reaction (10). Reactions (2), (3) and (6) are also expected to occur. Simonaitis and Heicklen [13] reported:

$$O(^1D) + H_2O = 2OH \tag{10}$$

that >90% of the $O(^1D) + H_2O$ reaction occurs by reaction (10). Using $k_{10} = 4.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [6], $R_9/R_{10} = 0.017$, and $R_3/R_{10} = 0.025$, showing that $O(^1D)$ reacts almost solely with water, and the resulting OH reacts entirely with C_3H_6. Oxygenated compounds were only found in series (1), where 19 products have been detected, and 6 remain unidentified. This attests to the enormous complexity of the NO_2 system, probably because of free radical–NO_2 or free radical–NO reactions. Some of the unidentified compounds almost certainly contained nitrogen, but we have not attempted to characterize them because they are not important to the objective of this communication. Because of its complexity, the $NO_2/H_2/C_3H_6$ system appears unsuitable for quantitative study of the OH–propylene reaction, and we are not pursuing it further at this time.

It is important to note that 1,5-hexadiene is formed in each of the three series. It can be most easily explained by dimerization of allyl radicals:

$$2 \text{ CH}_2 \relbar\joinrel\relbar \text{ CH} \relbar\joinrel\relbar \text{ CH}_2 = 1,5\text{-}C_6H_{10} \tag{11}$$
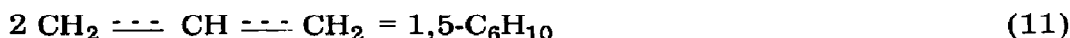
Allyl radicals can conceivably be formed by reaction of either OH, H, or $O(^1D)$ with C_3H_6. The importance of abstraction by these species, relative to the overall OH + C_3H_6 reaction, was calculated from the expressions, $R_{12}/R_6 = k_{12}[O(^1D)]/k_6[OH]$, and $R_{13}/R_6 = k_{13}[H]/k_6[OH]$, where reactions (12) and (13) are:

$$O(^1D) + C_3H_6 = OH + C_3H_5 \tag{12}$$
$$H + C_3H_6 = H_2 + C_3H_5 \tag{13}$$
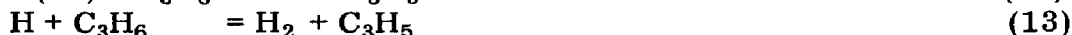
The ratios of the steady state concentrations of H, OH, and $O(^1D)$ were approximated by using only the primary reactions listed above for each series in the computations. Then using $k_6 = (1 \pm 0.5) \times 10^{-11} \text{ cm}^3$ molecule^{-1} s^{-1} [9], $k_{13} = 4.2 \times 10^{-16} \text{ cm}^3$ molecule^{-1} s^{-1} [14], and $k_{12} = 1.0 \times 10^{-10} \text{ cm}^3$ molecule^{-1} s^{-1}, $R_{13}/R_6 = 2.4 \times 10^{-5}$, 0.04 and 0.0 in series (1), (2) and (3), respectively, while $R_{12}/R_6 = 0.015$, 0.008 and 0.015, in aeries (1), (2) and (3) respectively. Assuming that every allyl

radical formed in reaction (13) yields 1,5-hexadiene (an obvious over-estimate), and that the rest of the measured products account for all of the OH which reacts with propylene, the upper limit yield of 1,5-hexadiene predicted to be formed as a consequence of H atom reactions is 1.2×10^{-3} % in series (1), 2% in series (2) and none in series (3). Since observed 1,5-hexadiene yields are larger than the predictions, additional sources of allyl must exist. Reaction (13) may play a role at least in series (2), since the increased 1,5-hexadiene yield correlates with [H]/[OH], which is calculated to be 0.6 in series (1) and 1.1×10^3 in series (2). This is expected since the H atoms generated in reaction (1) of series (2) must react almost exclusively with propylene instead of NO_2, as in series (1). Thus the method of series (2), while perhaps superior to that of series (1), is not entirely satisfactory because of the effects of H atoms.

The H + C_3H_6 reaction cannot explain 1,5-hexadiene yields in series (3) because H is not formed in any of the initial steps of the reaction, and there is no evidence for H formation in later stages. The relative rate calculations above predict that 1,5-hexadiene yields arising through reaction (12), followed by dimerization of all allyls so formed is 1.5%, 0.8% and 1.5% in series (1), (2) and (3), respectively. These are gross overestimates, since k_{12} was assumed to equal the collision frequency, and all allyls assumed to recombine. Although the bimolecular rate coefficient for the overall $O(^1D)$ reaction with propylene may be this large, the allyl-producing channel is undoubtedly only a fraction of the total reaction, and the actual 1,5-hexadiene yields arising from reaction (12) must be less than computed above. Since the observed 1,5-hexadiene yields are significantly larger than the predictions of the sum arising through reactions (12) and (13), an OH–C_3H_6 reaction is indicated as a source of allyl radicals. This conclusion seems best for series (3), which is the "cleanest" method used. The large 1,5-hexadiene yield in series (2) is puzzling, however, since it is probably greater than can be accounted for by reactions (12), (13) and (14). Addition of OH to C_3H_6 at the double bond is exothermic by (35 ± 1) kcal/mol, and since a crude estimate of the adduct lifetime places it at $>10^{-9}$ s, collisional stabilization must occur at 1 atm. It seems reasonable to assume that any allyl production in the OH–propylene reaction must occur by an abstraction reaction, rather than by decomposition of a chemically activated intermediate:

$$OH + C_3H_6 = H_2O + CH_2 \text{---} CH \text{---} CH_2 \tag{14}$$
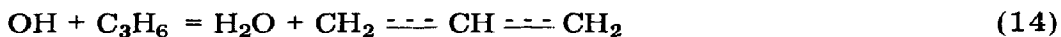
If the entire yield of 1,5-hexadiene in series (3) is attributed to reaction (14), followed by (11), k_{14} can be estimated from $k_{14}/2k_6 = 0.04$. If $k_6 = 1. \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, then $k_{14} = 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This is an underestimate, since other mechanisms for loss of allyl undoubtedly occur. A bond energy–bond order calculation of k_{14} has given $k_{14} = 1.7 \times 10^{-11}$ exp (−1737/RT) cm^3 molecule^{-1} s^{-1} [15], which at 500 °K gives $k_{14} = 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. This calculation corroborates the above kinetic analysis in that a relatively facile H-atom

abstraction is predicted, and furthermore the agreement between the theoretical and experimental estimates of k_{14} is reasonable, considering the heavy approximation involved in the experimental estimate of k_{14}. Although we feel that the experimental evidence provides a good argument for the occurrence of reaction (14), its importance relative to addition needs further investigation.

The method of series (3) is certainly the most suitable of those investigated here for studies of the OH−propylene mechanism. In order to suppress $O(^1D)$−propylene reactions, a large $[H_2O]/[C_3H_6]$ ratio is required and temperatures greater than 300 °K are needed to provide the necessary partial pressure of H_2O. This appears to be the principal drawback, since for application to smog, data in the vicinity of 300 °K would be more useful.

In series (2) and (3) the absence of oxygenated products, which have been previously observed [16], deserves comment. In series (2), the large steady state concentration of H could conceivably play a role suppressing or removing such products, while in series (3), H_2O condensation and subsequent dissolution of polar species could have occurred in the unheated g. c. sampling system.

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