

## A KINETIC STUDY OF THE REACTION OF OH WITH OLEFINS

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### Introduction

There is considerable interest in the rates and mechanism of the reactions of hydroxyl radicals with olefins because of their importance to the chemistry of the atmosphere and in combustion processes. However, the reported values of the reaction with propylene vary by a factor of  $\sim 5$ .<sup>1)</sup> In a preliminary study of this reaction, using the flash photolysis-resonance absorption technique, with OH produced by photolysis of H<sub>2</sub>O ( $\lambda > 160$  nm), we found that radicals from the photolysis of propylene were involved in secondary reactions with OH, thereby affecting the measured rates. In the present study we have produced OH by photolysis of N<sub>2</sub>O/H<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> mixtures at  $\lambda > 200$  nm. Under our experimental conditions the OH concentration was low and the photolysis of C<sub>3</sub>H<sub>6</sub> was reduced considerably and therefore the influence of secondary reactions was minimized. We have also assessed the effect of such secondary reactions by measurement of upper limits of the concentrations of the radicals present, and numerical simulation of the reactions involved and have established the magnitude of such an effect.

### Experimental

The apparatus and technique have been described in detail elsewhere.<sup>2,3)</sup> OH radicals were produced by photolysis of N<sub>2</sub>O/H<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> mixtures.<sup>2,3)</sup> A filter 8 mm deep of O<sub>2</sub> at 600 torr was used to cut radiation below  $\sim 200$  nm. O(<sup>1</sup>D) atoms from the photolysis of N<sub>2</sub>O react with H<sub>2</sub> to give OH which then reacts with H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>. The pressures of N<sub>2</sub>O, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> were such that virtually all the O(<sup>1</sup>D) atoms reacted with H<sub>2</sub> but not with N<sub>2</sub>O or C<sub>3</sub>H<sub>6</sub>.

Hydroxyl radicals were monitored by following the time resolved attenuation of the OH resonance radiation (Q<sub>1</sub><sup>3</sup> rotational line of the (0,0) band of the A<sup>2</sup> $\Sigma^+$   $\rightarrow$  X<sup>2</sup> $\Pi$  transition) at 308.2 nm produced by a microwave discharge in a low pressure Ar/H<sub>2</sub>O mixture. Signal averaging was used to improve the signal to noise ratio. The olefin concentrations were such that the measured pseudo-first order rates were 1 to  $5 \times 10^4$  s<sup>-1</sup>.

Gas chromatographic (G.C.) analyses of the reaction mixtures were made on a squalane modified alumina column with a flame ionization detector.

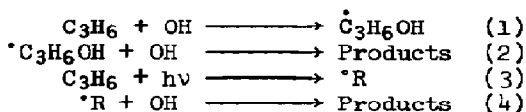
### Results

The optimum experimental conditions were established by G.C. determination of the amount of C<sub>3</sub>H<sub>6</sub> consumed per flash both by reaction with OH and by photolysis, for reaction mixtures corresponding to our range. These were: a single flash of low energy ( $\sim 150$  J) per mixture. We also obtained from these analyses the approximate amount of OH formed per flash, i.e.  $[\text{OH}]_0 \approx 10^{-11}$  mol cm<sup>-3</sup>, (which agrees well with that calculated from the initial absorption of the resonance radiation), and the approximate amount

of radicals [R] formed per flash from the photolysis of  $C_3H_6$ , i.e.  $[R] \approx 0.4\%$  of  $[C_3H_6]$ .

The second order rate constant obtained was  $k_{C_3H_6} = 1.47 \pm 0.08 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  where the uncertainty is one standard deviation. It agrees well with the higher values of previous determinations.<sup>1)</sup>

As mentioned in the introduction, possible sources of systematic errors in the present system are radical-radical reactions involving OH, i.e.,



Maximum values of these errors in each one of our experiments were estimated by numerical simulation of the reactions for the following conditions:

- (1) The measured values of  $[OH]_0$  and  $[R]$  were used, i.e.  $[OH]_0 \approx 10^{-11} \text{ mol cm}^{-3}$  and  $[R] \approx 0.4\%$  of  $[C_3H_6]$ .
- (2) The rate constants  $k_2$  and  $k_4$  were taken to be equal to the collisional rate,  $k_2 \approx k_4 \approx 2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .
- (3) The calculation was made for OH decays in the range of the actual observations. The overall systematic error in  $k_{C_3H_6}$  was estimated to be less than 10%.

These measurements will be extended to other olefins.

#### References

- 1) R. Atkinson, and J.N. Pitts, Jr. J. Chem. Phys. 63, 3591 (1975) and references therein.
- 2) R.P. Overend, G. Paraskevopoulos and R.J. Cvetanovic, Can. J. Chem. 53, 3374 (1975).
- 3) R. Overend and G. Paraskevopoulos, J. Chem. Phys. 67, 674 (1977).