

# C<sub>3</sub>H<sub>6</sub> + OH and C<sub>3</sub>D<sub>6</sub> + OH: Addition-Elimination vs. Abstraction Reaction

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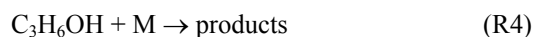
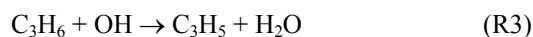
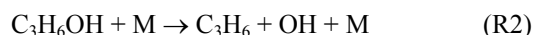
## Abstract

The reactions of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>D<sub>6</sub> with OH were studied in the temperature range 600–725 K at pressures from 10 to 30 bar with helium as the bath gas. The OH-radical concentration-time profiles were monitored by laser-induced fluorescence (LIF). From the observed biexponential intensity-time profiles and master-equation calculations, rate coefficients for OH-addition and abstraction of H and D atoms, respectively, were obtained.

## Introduction

Unsaturated hydrocarbons are essential constituents of gasoline and liquefied petroleum gases and are also formed *in situ* during the oxidation of alkanes. Propene as the smallest hydrocarbon with both a double bond and abstractable hydrogen atoms in allylic position may serve as a prototypical example to study radical attack *e.g.*, by OH. Like many other reactions relevant in combustion, OH + C<sub>3</sub>H<sub>6</sub> is a multi-channel reaction with a complex-forming step. Rate coefficients for this kind of reaction usually show a complicated temperature and pressure dependence, which makes extrapolations to other temperature and pressure ranges a difficult task.

For the OH + C<sub>3</sub>H<sub>6</sub> reaction, many studies at low temperatures (below ~500 K) have been carried out [1–3]. It is widely accepted [1, 2] that at these temperatures the reaction proceeds via addition of the OH radical to the double bond to form an adduct C<sub>3</sub>H<sub>6</sub>OH. When the temperature is increased, other reaction channels become competitive: the adduct C<sub>3</sub>H<sub>6</sub>OH can dissociate backwards to the reactants or forward to products, and H abstraction from C<sub>3</sub>H<sub>6</sub> can become important. The general reaction scheme can be written as:



The kinetic behavior becomes less complicated again, when the temperature is further increased (above ~700 K), because then abstraction is the predominant channel [1, 2]. This high-temperature region was investigated only in a few studies [4–7].

In the current work, we present experiments on the C<sub>3</sub>H<sub>6</sub> + OH reaction in the intermediate temperature range between 600 and 700 K. From these experiments, we determine rate coefficients for both the addition reaction and the abstraction reaction. The C<sub>3</sub>D<sub>6</sub> + OH reaction was also studied, because a different isotope effect on the abstraction and the addition can be expected. The experimental results were analyzed by using rate coefficients  $k_2$  and  $k_4$  calculated from

statistical rate theory with molecular data from quantum chemical calculations.

## Experimental

**Experimental Setup and Conditions.** Since the experimental setup was described in detail elsewhere [8, 9], only a brief summary is given here. The reactions were investigated in a quasi-static reactor in a temperature range from 600 to 725 K at pressures ranging from 10 to 30 bar with helium as the bath gas. The initial concentrations were chosen so as to ensure pseudo-first order conditions for OH with respect to C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>D<sub>6</sub>, respectively ( $[\text{HNO}_3]_0 = (8\text{--}36) \times 10^{15} \text{ cm}^{-3}$  resulting in  $[\text{OH}]_0 \sim (1\text{--}8) \times 10^{12} \text{ cm}^{-3}$ ,  $[\text{C}_3\text{H}_6]_0 = (1.1\text{--}7.5) \times 10^{16} \text{ cm}^{-3}$ , and  $[\text{C}_3\text{D}_6]_0 = (2.5\text{--}7.2) \times 10^{16} \text{ cm}^{-3}$ ). The OH radicals were produced by laser-flash photolysis of HNO<sub>3</sub> at 248 nm by using a KrF-excimer laser (Compex 102, Lambda Physik). The fluorescence of OH was excited at a wavelength of 281.9 nm by a dye laser, which was pumped by a XeCl-excimer laser (Scanmate 1E with Coumarin 153, Lambda Physik and Compex 102, Lambda Physik, respectively); the wavelength range for detection was  $(308 \pm 7.5) \text{ nm}$ . Under these experimental conditions, the observed intensity-time profiles showed a biexponential behavior as is displayed in Fig. 1.

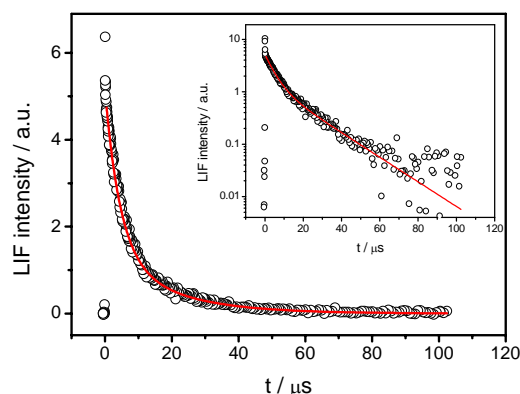


Fig. 1. Intensity-time profile of the OH fluorescence and biexponential fit according to eq. 1 ( $T = 667 \text{ K}$ ,  $P = 22.8 \text{ bar}$ ,  $[\text{HNO}_3]_0 = 6.9 \times 10^{15} \text{ cm}^{-3}$ ,  $[\text{C}_3\text{H}_6]_0 = 1.6 \times 10^{16} \text{ cm}^{-3}$ ).

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## Data Analysis

Since under our conditions, all the reactions in the above mechanism, eq. R1–R4, are (pseudo-)first order, the rate law for  $[\text{OH}](t)$  can be obtained by analytical integration (see *e.g.*, [10]); one obtains:

$$\frac{[\text{OH}]}{[\text{OH}]_0} = \frac{I}{I_0} = \frac{1}{\lambda_2 - \lambda_1} \times \frac{1}{[(\gamma - \lambda_1)\exp(-\lambda_1 t) - (\gamma - \lambda_2)\exp(-\lambda_2 t)]} \quad (1)$$

where  $\gamma = k_2 + k_4$ ,  $\lambda_{1,2} = \{(k_1' + k_2 + k_3' + k_4) \pm [(k_1' + k_2 + k_3' + k_4)^2 - 4c]^{1/2}\} / 2$ ,  $c = k_1'k_4 + k_2k_3' + k_3'k_4$ , and  $k_i' = k_i[\text{C}_3\text{H}_6]$ .

Parameter estimations for such biexponential decays should be done with care [11]. In particular, it is not reasonable to fit all four rate coefficients occurring in eq. 1 to experimental fluorescence-time profiles of the kind shown in Fig. 1. Therefore, we calculated the rate coefficients for the two dissociation pathways of the adduct  $\text{C}_3\text{H}_6\text{OH}$ ,  $k_2(T, P)$  and  $k_4(T, P)$ , separately by solving a chemical activation master equation with input data from quantum chemical calculations [12]. Under our experimental conditions, the rate coefficients obtained were virtually independent of pressure, and their temperature dependence can be expressed in the following way (for  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{D}_6$ , respectively):

$$k_2(T) = 5.45 \times 10^{13} \exp(-13500 \text{ K}/T) \text{ s}^{-1} \quad (2)$$

$$k_4(T) = 8.76 \times 10^{13} \exp(-15830 \text{ K}/T) \text{ s}^{-1} \quad (3)$$

$$k_{2,D}(T) = 5.41 \times 10^{13} \exp(-13440 \text{ K}/T) \text{ s}^{-1} \quad (4)$$

$$k_{4,D}(T) = 1.06 \times 10^{14} \exp(-15920 \text{ K}/T) \text{ s}^{-1} \quad (5)$$

These rate coefficients were inserted into eq. 1 for a given temperature  $T_{\text{exp}}$  and kept fixed during the fitting procedure resulting in the rate coefficients  $k_1(T_{\text{exp}})$  and  $k_3(T_{\text{exp}})$ .

## Results and Discussion

**$\text{C}_3\text{H}_6 + \text{OH}$ .** The results for the rate coefficients  $k_1(T)$  and  $k_2(T)$  are shown in Figs. 2 and 3, respectively. The temperature dependences in the range  $T = 600$ – $700$  K can be expressed as follows:

$$k_1(T) = 5.7 \times 10^{-13} \exp(940 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1} \quad (6)$$

$$k_3(T) = 3.0 \times 10^{-9} \exp(-4270 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1} \quad (7)$$

In Figs. 2 and 3, our values are also compared with results of Tully and Goldsmith [4], the study, which was performed at conditions most closely to ours. These authors determined rate coefficients in the temperature ranges  $T = 293$ – $480$  K and  $T = 700$ – $896$  K. In the lower of the two temperature ranges, monoexponential decays of the OH concentration were observed and assigned completely to the addition channel, reaction R1 [4]. At pressures between 250 and 800 mbar, no discernible

pressure dependence was found. Atkinson in his review [1] concluded that in the temperature range 300–420 K at pressures near 1000 mbar, the  $\text{C}_3\text{H}_6 + \text{OH}$  reaction is almost completely governed by the addition channel R1, and that the rate coefficient is close to its high-pressure limit deviating by at most 10%. Since on the basis of the above mechanism, eq. R1–R4, our results obtained for  $k_1$  correspond to high-pressure limiting values, the match with the data from ref. 4 seems reasonable as can be realized from Fig. 2. The negative temperature dependence found in ref. 4 for temperatures below 500 K is confirmed by our experiments to extend into the temperature range 600–700 K.

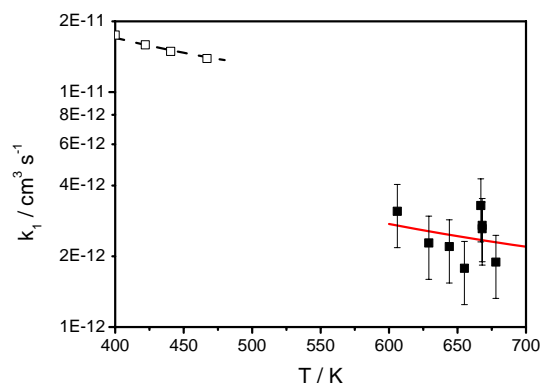


Fig. 2. Experimental results for  $k_1$ ; full squares: this work, red line: Arrhenius fit (eq. 6), open squares and dashed line: ref. 4.

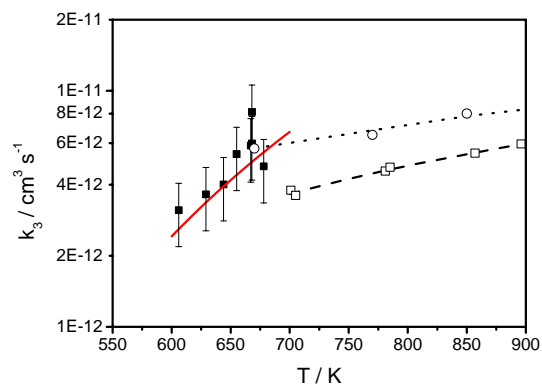


Fig. 3. Experimental results for  $k_3$ ; full squares: this work, red line: Arrhenius fit (eq. 7), open squares and dashed line: ref. 4, open circles and dotted line: ref. 6.

At temperatures above 700 K, Tully and Goldsmith [4] again observed monoexponential OH decays, which probably can be attributed to the hydrogen abstraction reaction, eq. R3 [1, 2, 4–7]. As can be realized from Fig. 3, our results for the rate coefficient  $k_3$  reasonably match the data from refs. 4 and 6 obtained in the adjacent temperature range.

**C<sub>3</sub>D<sub>6</sub> + OH.** For the reaction of OH with propene-d<sub>6</sub>, biexponential behavior was observed in the temperature range 640–725 K. Our data analysis was again based on reactions R1–R4 with rate coefficients for R2 and R4 from master equation calculations, which are given by eq. 4 and 5. Since the addition of OH to the double bond is not expected to show a significant isotope effect, when C<sub>3</sub>H<sub>6</sub> is exchanged against C<sub>3</sub>D<sub>6</sub> [4], we adopted the rate coefficient  $k_1$  as obtained from the analysis of the C<sub>3</sub>H<sub>6</sub> + OH reaction, that is, we set  $k_{1,D}(T) = k_1(T)$ . In this way, the only remaining fit parameter is  $k_{3,D}$ , the rate coefficient for D abstraction, eq. R3. The results we obtained are displayed in Fig. 4, and the temperature dependence can be expressed in the form

$$k_{3,D}(T) = 1.0 \times 10^{-15} \exp(5940 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1} \quad (8)$$

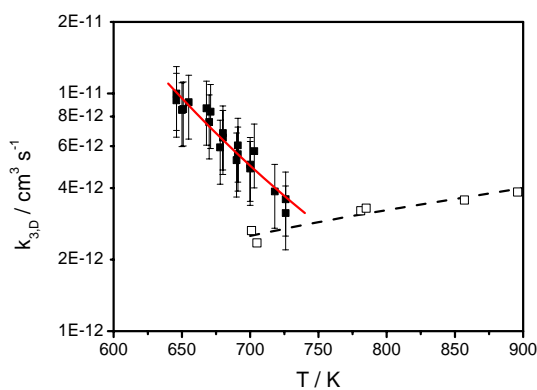


Fig. 4. Experimental results for  $k_{3,D}$ ; full squares: this work, red line: Arrhenius fit (eq. 8), open squares and dashed line: ref. 4.

The values for  $k_{3,D}$  we obtained are, though a little bit larger, in the same order of magnitude as those for the H abstraction from C<sub>3</sub>H<sub>6</sub>. The most unexpected result, however, was that we were only able to fit our experimental fluorescence-time profiles with rate coefficients  $k_{3,D}(T)$  obeying a negative temperature dependence. This is in disagreement with the expected isotope effect for a direct abstraction reaction over a barrier as well as with the earlier results from Tully and Goldsmith [4] (see Fig. 4). We consider this result as preliminary and plan to perform further experiments and a refined data analysis, taking into account the possibility of an intermediate  $\pi$ -complex, HO-C<sub>3</sub>H<sub>6</sub> and HO-C<sub>3</sub>D<sub>6</sub>, respectively, through which both addition and abstraction can proceed [13].

## Summary and Conclusions

The reactions C<sub>3</sub>H<sub>6</sub> + OH and C<sub>3</sub>D<sub>6</sub> + OH were experimentally studied in the temperature range 600–725 K at pressures from 10–30 bar. In this temperature range, the rate coefficients of these reactions are known [1, 2, 4, 6] to exhibit a complicated temperature dependence probably due to the competition between OH addition and H abstraction. In the present work the rate coefficients of the competing channels were separated by analyzing the biexponential fluorescence-time profiles of the OH radicals. The temperature dependences were parametrized in Arrhenius form.

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