# Rate constants for the reactions of ozone with ethene and propene, from 235.0 to 362.0 K

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# Rate Constants for the Reactions of Ozone with Ethene and Propene, from 235.0 to 362.0 K

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The rate constants for the reactions of ozone with ethene and propene have been measured over the temperature range 235.0–362.0 K, using a stopped-flow system coupled to a beam-sampling mass spectrometer. The rate constants found, at a total pressure of about 500 N m$^{-2}$, in the presence of molecular oxygen, were $k(C_2H_4) = (5.42 \pm 3.19) \times 10^9 \exp(-2557 \pm 167/T)$ cm$^3$ mol$^{-1}$ sec$^{-1}$ and $k(C_3H_6) = (3.70 \pm 1.42) \times 10^9 \exp(-1897 \pm 109/T)$ cm$^3$ mol$^{-1}$ sec$^{-1}$.

## Introduction

Although there have been numerous studies of the kinetics of the ozone–olefin reactions at room temperature (see Stedman, Wu, and Niki[1] and references therein), there are few data available at other temperatures, the only extensive set of data being that of DeMore[2] on C$_2$H$_2$ (243–283 K), C$_2$H$_4$ (178–233 K), and C$_3$H$_6$ (183–193 K). We report here data on the kinetics of the reaction of ozone with C$_2$H$_4$ and C$_3$H$_6$ over the temperature range 235.0–362.0 K.

## Experimental Section

The experiments were carried out using a stopped-flow reactor, shown in Figure 1, coupled to a beam-sampling mass spectrometer.[3,4] Ozone, produced in an ozonizer and stored at –78° on silica gel, was mixed with reactant olefin and carrier gas (Ar or O$_2$) and was allowed to flow into a 350-cm$^3$ glass reactor. Flow into and out of the reactor was controlled by stainless steel solenoid valves, which could be closed simultaneously to entrap the premixed reacting gases. The contents of the reactor were monitored by means of a beam-sampling mass spectrometer through a 100-$\mu$m diameter orifice. A modulated ion signal was obtained by mechanically chopping the beam, and a phase-sensitive detection technique was used. The output of the phase-sensitive amplifier was digitized, sampled at a preselected interval, and stored on a paper tape using a high-speed punch. The reactor was double-walled so that fluid could be circulated to cool or heat the reactor. The temperature of the reactor was measured by means of a copper-constantan thermocouple inserted into the reactor through a "well" (see Figure 1). The temperature of the circulating heat-exchange liquid was also measured using a copper–constantan thermocouple or an immersion thermometer. The two temperatures were identical under all experimental conditions. The uncertainty in temperature measurement was less than 0.5 K and resulted primarily from potentiometer reading error. The total pressure was about 500 N m$^{-2}$ and was measured by means of a capacitance manometer. The sensitivity of the mass spectrometer to the olefins was determined for each run using two different gas mixtures of known composition (2–5% olefin in O$_2$).

## Results

For the reaction of ozone with an olefin A

$$O_3 + A \longrightarrow \text{products}$$
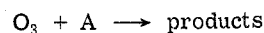
$$-d[O_3]/dt = k_1[O_3][A] \qquad (1)$$

and if $[A] \gg [O_3]$, then

$$\ln [O_3] = k_1[A]t + c$$

where $k_1[A]$ is effectively the first-order rate constant for the decay of ozone in excess olefin. The ozone decay data, in digital form, corrected for any background ion signal at $m/e$ 48, were fitted to eq 1 using a weighted linear least-squares routine. The weighting function used was $W = (N - B)^2/(N + B)$, where $N$ is the signal intensity and $B$ is the background correction. The slopes from these fits are the first-order rate constants given in Tables I and II. The stat-

**TABLE I: Rate Data for the Reaction of Ozone with Ethene**

| $T$, K | $10^9[C_2H_4]_0$, mol cm$^{-3}$ | $10^9[O_3]_0$, mol cm$^{-3}$ | $10^2 k^{1st}$, sec$^{-1}$ |
|---|---|---|---|
| 235.0 | 0.0 | 0.16 | 0.258 ± 0.009 |
| | 3.32 | 0.12 | 0.350 ± 0.015 |
| | 7.72 | 0.17 | 0.350 ± 0.016 |
| | 14.0 | 0.15 | 0.461 ± 0.017 |
| | 27.8 | 0.14 | 0.671 ± 0.019 |
| | 39.9 | 0.16 | 0.784 ± 0.020 |
| | $k = (1.35 \pm 0.08) \times 10^5$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 266.9 | 0.0 | 0.19 | 0.267 ± 0.010 |
| | 2.33 | 0.20 | 0.342 ± 0.011 |
| | 5.18 | 0.17 | 0.467 ± 0.014 |
| | 8.79 | 0.20 | 0.591 ± 0.018 |
| | 12.31 | 0.19 | 0.683 ± 0.027 |
| | 17.13 | 0.19 | 0.853 ± 0.024 |
| | 20.87 | 0.18 | 0.988 ± 0.032 |
| | $k = (3.48 \pm 0.09) \times 10^5$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 286.2 | 0.0 | 0.12 | 0.380 ± 0.010 |
| | 1.82 | 0.12 | 0.488 ± 0.017 |
| | 3.73 | 0.14 | 0.601 ± 0.025 |
| | 6.30 | 0.13 | 0.659 ± 0.021 |
| | 9.24 | 0.13 | 0.909 ± 0.025 |
| | 14.6 | 0.11 | 1.29 ± 0.03 |
| | 26.3 | 0.14 | 1.83 ± 0.03 |
| | $k = (5.62 \pm 0.22) \times 10^5$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 309.4 | 0.0 | 0.15 | 0.264 ± 0.009 |
| | 1.84 | 0.16 | 0.600 ± 0.012 |
| | 3.79 | 0.16 | 0.830 ± 0.018 |
| | 5.62 | 0.16 | 1.09 ± 0.02 |
| | 7.41 | 0.16 | 1.29 ± 0.02 |
| | 9.21 | 0.17 | 1.59 ± 0.02 |
| | 11.3 | 0.16 | 1.88 ± 0.02 |
| | 14.5 | 0.15 | 2.29 ± 0.03 |
| | $k = (1.41 \pm 0.03) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 332.4 | 0.0 | 0.11 | 0.337 ± 0.008 |
| | 2.12 | 0.12 | 0.917 ± 0.023 |
| | 3.19 | 0.28 | 1.18 ± 0.01 |
| | 3.31 | 0.02 | 1.13 ± 0.06 |
| | 3.56 | 0.12 | 1.29 ± 0.03 |
| | 6.02 | 0.12 | 1.77 ± 0.03 |
| | 6.35 | 0.27 | 1.86 ± 0.02 |
| | 6.46 | 0.02 | 1.83 ± 0.09 |
| | 8.67 | 0.11 | 2.43 ± 0.04 |
| | 11.08 | 0.02 | 2.75 ± 0.11 |
| | 11.19 | 0.26 | 2.85 ± 0.03 |
| | 11.69 | 0.13 | 2.90 ± 0.04 |
| | $k = (2.31 \pm 0.05) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 362.0 | 0.0 | 0.15 | 0.445 ± 0.008 |
| | 1.55 | 0.12 | 1.39 ± 0.02 |
| | 2.52 | 0.19 | 1.94 ± 0.03 |
| | 4.74 | 0.19 | 3.10 ± 0.04 |
| | 6.45 | 0.14 | 3.93 ± 0.07 |
| | 9.07 | 0.20 | 5.24 ± 0.07 |
| | $k = (5.44 \pm 0.11) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |

**TABLE II: Rate Data for the Reaction of Ozone with Propene**

| $T$, K | $10^9[C_3H_6]_0$, mol cm$^{-3}$ | $10^9[O_3]_0$, mol cm$^{-3}$ | $10^2 k^{1st}$, sec$^{-1}$ |
|---|---|---|---|
| 250.0 | 0.0 | 0.16 | 0.258 ± 0.009 |
| | 1.24 | 0.12 | 0.378 ± 0.027 |
| | 3.16 | 0.15 | 0.632 ± 0.020 |
| | 4.73 | 0.14 | 0.859 ± 0.029 |
| | 6.44 | 0.15 | 1.04 ± 0.02 |
| | 8.78 | 0.17 | 1.36 ± 0.03 |
| | 17.2 | 0.13 | 2.41 ± 0.03 |
| | $k = (1.25 \pm 0.01) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 266.9 | 0.0 | 0.19 | 0.267 ± 0.010 |
| | 2.85 | 0.18 | 1.16 ± 0.02 |
| | 4.82 | 0.19 | 1.76 ± 0.03 |
| | 7.60 | 0.17 | 2.43 ± 0.04 |
| | 9.57 | 0.18 | 3.11 ± 0.05 |
| | 11.6 | 0.17 | 3.56 ± 0.05 |
| | $k = (2.91 \pm 0.06) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 286.2 | 0.0 | 0.12 | 0.380 ± 0.010 |
| | 1.31 | 0.11 | 0.914 ± 0.026 |
| | 2.31 | 0.11 | 1.29 ± 0.03 |
| | 3.64 | 0.12 | 2.00 ± 0.03 |
| | 5.55 | 0.12 | 2.95 ± 0.05 |
| | 7.36 | 0.14 | 3.63 ± 0.05 |
| | $k = (4.44 \pm 0.09) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 309.4 | 0.0 | 0.15 | 0.264 ± 0.090 |
| | 1.92 | 0.16 | 1.93 ± 0.04 |
| | 3.02 | 0.16 | 2.85 ± 0.04 |
| | 4.81 | 0.15 | 4.53 ± 0.07 |
| | 6.69 | 0.15 | 5.99 ± 0.09 |
| | 8.79 | 0.15 | 7.55 ± 0.10 |
| | $k = (8.50 \pm 0.11) \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 332.4 | 0.0 | 0.11 | 0.337 ± 0.080 |
| | 1.71 | 0.10 | 2.14 ± 0.03 |
| | 2.18 | 0.025 | 2.69 ± 0.12 |
| | 2.43 | 0.24 | 2.91 ± 0.03 |
| | 2.80 | 0.10 | 3.23 ± 0.05 |
| | 4.55 | 0.10 | 5.11 ± 0.07 |
| | 4.89 | 0.017 | 5.87 ± 0.39 |
| | 5.48 | 0.23 | 6.11 ± 0.06 |
| | 6.24 | 0.11 | 6.93 ± 0.11 |
| | $k = (1.06 \pm 0.01) \times 10^7$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |
| 362.0 | 0.0 | 0.15 | 0.445 ± 0.008 |
| | 1.10 | 0.14 | 3.20 ± 0.05 |
| | 1.89 | 0.18 | 4.81 ± 0.06 |
| | 2.82 | 0.18 | 7.00 ± 0.08 |
| | 3.89 | 0.16 | 9.24 ± 0.14 |
| | $k = (2.30 \pm 0.03) \times 10^7$ cm$^3$ mol$^{-1}$ sec$^{-1}$ | | |

ed uncertainties are the standard errors of the slopes from the least-squares fit. First-order rate constants were mea-sured over a range of olefin concentrations, keeping $[A]_0 > 10[O_3]_0$. Second-order rate constants at a particular temperature were determined as the slope of a plot of the first-order rate constant against the olefin concentration. The olefin concentration was corrected for effusion to a weighted midpoint of the reaction, $(N/N_0)^2 = \frac{1}{2}$. The correction factor was typically less that 1% and never exceeded 6%.
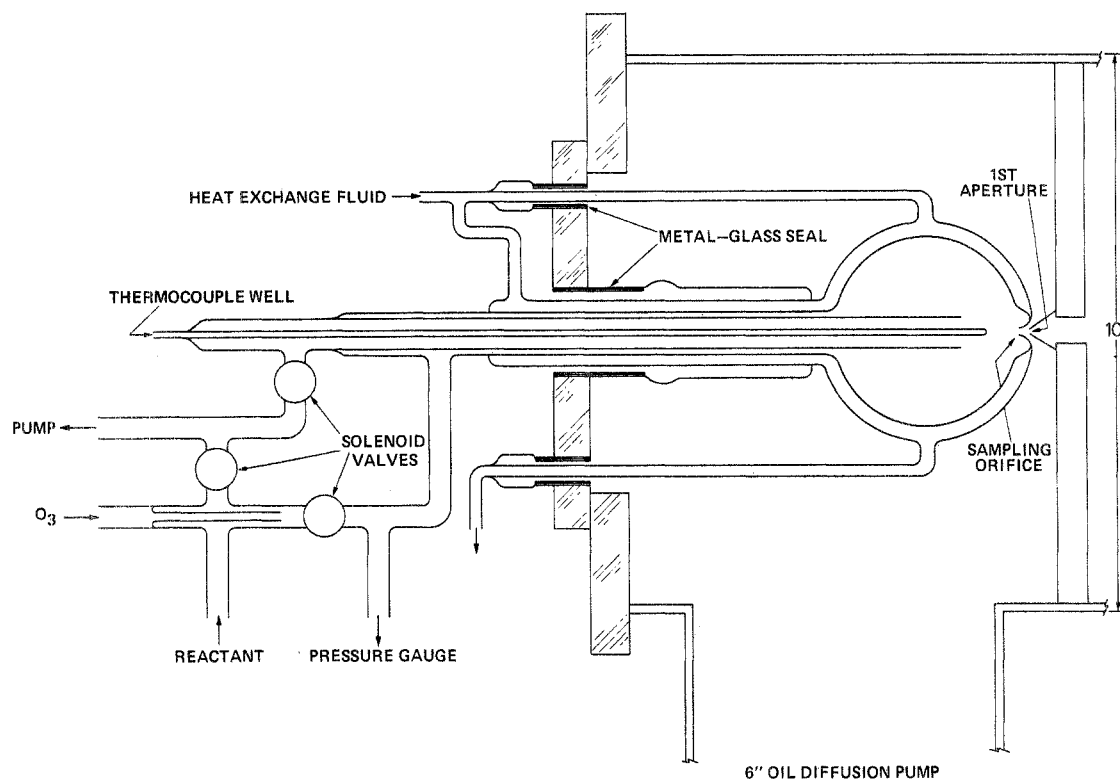
**Figure 1.** Stopped-flow reactor.

The second-order rate constants are shown in Arrhenius form in Figure 2. The error bars reflect both the uncertainty in the values from the least-squares standard error and an additional 5% uncertainty resulting from the calibration procedure. A least-squares fit of the data to the Arrhenius expression, weighted by the squares of the relative uncertainties of the second-order rate constants, gave

$$k(C_2H_4) = (5.42 \pm 3.19) \times$$
$$10^9 \exp(-2557 \pm 167/T) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$k(C_3H_6) = (3.70 \pm 1.42) \times$$
$$10^9 \exp(-1897 \pm 109/T) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

All the data used in the determination of these rate constants were obtained in the presence of about 400 N m$^{-2}$ of oxygen, which was used as the carrier gas. In most experiments the concentration of ozone was kept between about 1 and $2 \times 10^{-10}$ mol cm$^{-3}$ and the olefin concentration was varied. In the rate measurements at 332.4 K, however, measurements were made over a tenfold range of ozone concentrations. The first-order rate constants were found to be independent of ozone concentration.

In the initial studies on the kinetics of the olefin reactions in which argon was used as a carrier gas, we obtained results which were nonreproducible and led to rate constants much higher than those reported by other workers at room temperature and atmospheric pressure.[1] Since it is known[5,6] that free radicals are products of ozone–olefin reactions at low pressures, it seemed likely that secondary reactions of free radicals and ozone were the source of the anomalous results. In flow tube experiments under similar conditions, Niki[7] has observed that oxygen has a strong effect on the course of the reaction. This suggested the possi-
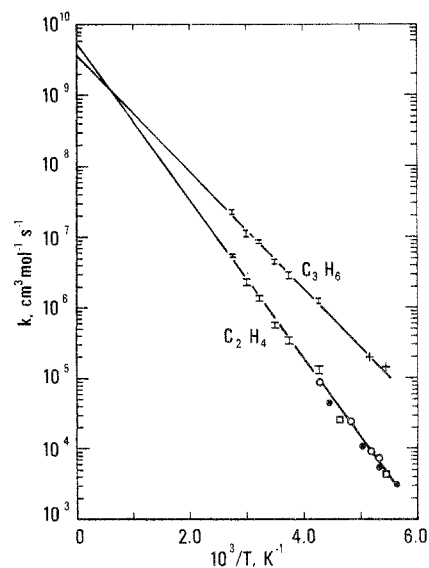


**Figure 2.** Arrhenius plot for the reactions of ozone with ethene and propene; data with error bars are from this work; other points are from ref 2: open circles, added oxygen; closed circles, inert gas, atmospheric pressure; open squares, inert gas, atmospheric pressure, and added oxygen; crosses, conditions not specified.

bility of scavenging the reactive free radicals with molecular oxygen.

Figure 3 shows the effect of added $O_2$ on the apparent second-order rate constant for the reaction of ozone with propene at room temperature. Similar results are found for other olefins. The effect of added $O_2$ is dramatic and appears to confirm the hypothesis that free radicals produced in the initial ozone–olefin reaction react rapidly with ozone. In the presence of excess $O_2$, the radicals are scavenged and the true rate constant is obtained.
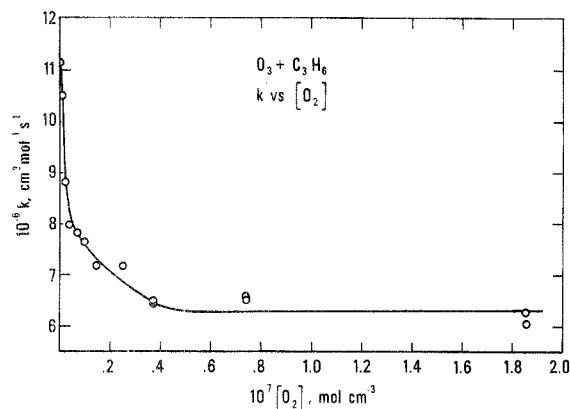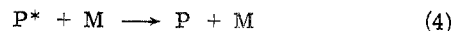
**Figure 3.** Effect of molecular oxygen on the apparent rate constant for the reaction of ozone with propene at 298 K and 450 N m$^{-2}$ total pressure.

## Discussion

The results obtained in this work can be compared with those of DeMore,[2] which are shown in Figure 2. In the work of DeMore, the reactions were carried out in an 86-cm$^3$ cell, following the ozone concentration by absorption at 253.7 nm. Measurements were made with added inert gases or $O_2$ at total pressure in excess of atmospheric or at lower total pressures (1.3–4 kN m$^{-2}$) with added $O_2$. As can be seen from Figure 2, our Arrhenius lines fit the data of DeMore very closely. Recent measurements by Stedman, *et al.*,[1] at room temperature and atmospheric pressure (with and without $O_2$) in which the ozone decay was monitored using a chemiluminescence ozone detector also give results in good agreement with the present values. Thus, Stedman, *et al.*, reported $k(C_2H_4) = 9.34 \times 10^5$ cm$^3$ mol$^{-1}$ sec$^{-1}$ and $k(C_3H_6) = 7.53 \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ while we calculate from our Arrhenius expression $k(C_2H_4) = 1.02 \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$ and $k(C_3H_6) = 6.36 \times 10^6$ cm$^3$ mol$^{-1}$ sec$^{-1}$.

The agreement in all cases is close and strongly supports our interpretation of the role of molecular oxygen at low pressures. These observations, together with the observations of other workers that $O_2$ has no effect on the rate constant for ozone loss at atmospheric pressure, suggest the general mechanism for these reactions

$$O_3 + A \longrightarrow P^* \qquad (2)$$

$$P^* \longrightarrow Q + R + \text{---} \qquad (3)$$

$$P^* + M \longrightarrow P + M \qquad (4)$$

$$O_3 + (Q + R + \text{---}) \longrightarrow \text{products} \qquad (5)$$

where P* is not necessarily the initially formed adduct but could be formed by its subsequent rearrangement. At low pressures reaction 3 is favored followed by reaction 5. At high pressures reaction 4 is favored and reaction 3 and 5 are unimportant. With added $O_2$ at low pressures

$$O_2 + (Q + R + \text{---}) \longrightarrow \text{products} \qquad (6)$$
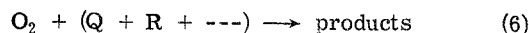
and again reaction 5 is unimportant.

An alternative explanation for the reduction of the rate constant with added $O_2$ is

$$O_3 + A \longrightarrow P + P' + \text{---} \qquad (7)$$

$$P + O_2 \longrightarrow O_3 + X \qquad (8)$$
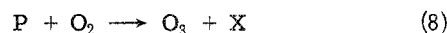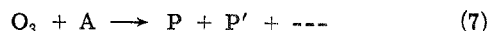
where P is an oxygen-containing free radical.

However, this mechanism is incompatible with the observations of Wu, *et al.*,[1] which showed that the stoichiometry of the reactions at atmospheric pressure with respect to reactant consumption was 1:1 with or without $O_2$. Also as noted above the rate constants are unaffected by $O_2$. Thus reaction 8 is very unlikely.

## References and Notes

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