# Rate Constant for the Reaction of OH Radicals with Isoprene at 298 ± 2 K

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Using the relative-rate technique, the rate constant for the reaction of OH radicals with isoprene was determined in one atmosphere of air at 298 ± 2 K. Methyl nitrite photolysis in air was used as a source of OH radicals. Ozone and O-atom reactions with isoprene were confirmed to have a negligible contribution on the loss of isoprene. The rate constant relative to three reference compounds yielded $(10.4 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (the uncertainty is $2\sigma$).

Isoprene is a dominant biogenic hydrocarbon and its emission is known to be primarily diurnal; the emission rate increases with increasing the light intensity and temperature, while in the dark, it is low regardless of the temperature.[1] The mixing ratios of isoprene and its oxidation products (methyl vinyl ketone and methacrolein) observed at rural measurement sites in or near forests showed a diurnal pattern, i.e., high during the day and low at night.[2] These results suggest that the reaction with OH, reaction (1), is the dominant atmospheric removal pathway for isoprene, while the NO$_3$ and O$_3$ can also initiate the oxidation of isoprene.

$$OH + isoprene \rightarrow products \qquad (1)$$

Reaction (1) can also be an important OH sink under certain conditions.[3] Therefore, the accurate kinetic data on reaction (1) are useful for atmospheric modeling.

Recently, four absolute-rate measurements using laser-induced fluorescence[4–6] and chemical ionization mass spectrometry[7] for the detection of OH radicals were reported. However, the measured rate constants for reaction (1) at room temperature were relatively scattered, from 11 at 0.27 kPa of He[4] to 8.4 at 16 kPa of He, N$_2$, and air,[6] in all the units of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In the absolute-rate measurements, the error in the absolute isoprene concentration, as well as the presence of secondary reactions generating or removing OH radicals, may be possible sources of error in $k_1$. On the other hand, the relative-rate technique need not determine the absolute concentration of isoprene. Furthermore, the secondary reactions leading to the additional formation or loss of OH radicals do not affect the relative-rate measurements. On the other hand, any side reactions consuming the target and/or reference compounds could interfere with the measurements of the relative rates, whose contribution has to be checked.

In the present work, we measured the rate constant for reaction (1) using the relative-rate method. A 6-m$^3$ photochemical reaction chamber was used for all of the experiments. Details concerning this chamber were reported previously.[8] Isoprene, references, and other chemicals were monitored by using a Fourier Transform Infrared Spectrometer. Multi-reflection using 128 separate paths provided a 221.5-m path length. As an irradiation light source, a solar simulator (19 × 1-kW Xe-arc
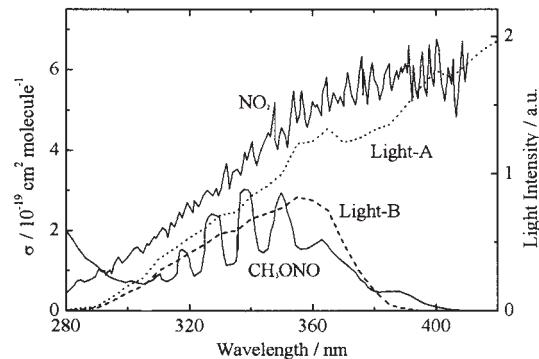


**Figure 1.** Solid lines are the absorption spectra of NO$_2$ and methyl nitrite taken from Ref. 12. Relative spectral distributions of filtered light sources, light-A (dotted line) and light-B (broken line). See text.

lamps) was used with two different sets of filters: a Pyrex filter (light-A) and a Pyrex + a band-pass (Hoya U-340) filters (light-B) for each lamp. The spectral distributions of the output of the solar simulator under light-A and light-B conditions and the absorption spectra of NO$_2$ and CH$_3$ONO, the OH radical source in the present work, are shown in Figure 1. The relative photodissociation rate, $J_{CH_3ONO}/J_{NO_2}$, was determined to be 0.2 with light-A and 0.45 with light-B. OH radicals were generated by the photolysis of methyl nitrite in purified air.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
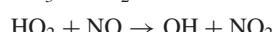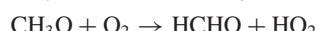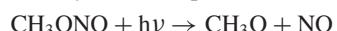
The experiments were conducted at 1 atm and 298 ± 2 K. Assuming that isoprene and references are consumed only by the reaction with OH radicals,

$$OH + isoprene \rightarrow products \qquad (1)$$

$$OH + reference \rightarrow products, \qquad (2)$$

and the data were analyzed according to equation (3).

$$\ln\{[isoprene]_0/[isoprene]_t\} =$$
$$(k_1/k_2) \times \ln\{[reference]_0/[reference]_t\} \qquad (3)$$

where $[X]_0$ and $[X]_t$ are the concentrations of X at times $t = 0$ and $t$, respectively, and $k_1$ and $k_2$ are the second-order rate constants for reactions (1) and (2), respectively. As references, cyclohexane, di-$n$-butyl ether, and propene were used because their OH reaction rate constants were well established.[9,10] The initial concentrations of CH$_3$ONO, NO, and organics (isoprene and references) were 0.5–3, 0.2–6, and 0.2–1 ppm, respectively.

Isoprene is known to react not only with OH radicals but also with O$_3$ and O atoms.

$$O_3 + isoprene \rightarrow products \qquad (4)$$

$$O + isoprene \rightarrow products \qquad (5)$$
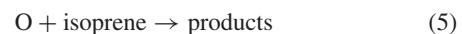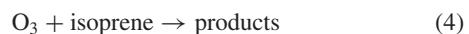
This suggests that the value of $k_1$ might include systematic errors, if reactions (4) and (5) compete with reaction (1). In all of the experiments, the contributions of reactions (4) and (5) to the total removal of isoprene were calculated to be $\leq 0.5\%$ and $\leq 6\%$, respectively, using the estimated steady-state concentrations of $O_3$ and O and the reported rate constants of reactions (4) and (5), $1.2 \times 10^{-17}$ and $3.5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.[10,11] However, relatively large uncertainties in $J_{NO_2}$, $k_4$, and $k_5$ (20–30%) considered, the contributions of reactions (4) and (5) should be checked experimentally.

The use of three reference organics would serve to check the contribution of $O_3$ reactions. Among the reference organics used in the present work, cyclohexane and di-$n$-butyl ether react exceedingly slowly with $O_3$. On the other hand, propene is known to react with $O_3$ with a rate constant similar to that of isoprene,[10] while its OH reaction rate constant seems to be smaller than that of isoprene based on the observed $k_1/k_2$ values. Hence, if $O_3$ reactions contribute to the loss of isoprene and propene, the value of $k_1$ must be overestimated when cyclohexane and di-$n$-butyl ether are used as a reference and underestimated when propene is used. The $k_1$ values obtained, however, showed no significant extent among the three reference systems as listed in Table 1. Therefore, the $O_3$ reactions were confirmed to be negligible in our relative-rate measurements.

Since all of the references used in the present work react with O atoms much more slowly than isoprene does, the influence of reaction (5) on relative-rate measurements could be checked by changing the $[O]_{ss}/[OH]_{ss}$ ratios, where $[X]_{ss}$ represents the steady-state concentration of species X. Since $[O]_{ss}$ is proportional to $J_{NO_2}$, while $[OH]_{ss}$ should be proportional to $J_{CH_3ONO}$, the ratio of $[O]_{ss}/[OH]_{ss}$ can be controlled by changing $J_{CH_3ONO}/J_{NO_2}$. According to this idea, experiments were conducted using light-B in place of light-A. As summarized in Table 1, the relative rates, $k_1/k_2$, obtained under the different irradiation conditions are in good agreement with each other for all sets of isoprene/reference pairs. This suggests that the presence of reaction (5) had no significant impact on our relative-rate measurements.

**Table 1.** Summary of relative-rate measurements

| Exp | Ref. compound | Light[a] | $k_1/k_2$[b] | $k_1/10^{-11}$[c] |
|---|---|---|---|---|
| 1 | Cyclohexane | A | $14.3 \pm 1.2$ | $10.3 \pm 1.2$ |
| 2 | Cyclohexane | B | $14.9 \pm 1.3$ | $10.7 \pm 1.3$ |
| 3 | di-$n$-Butyl ether | A | $3.71 \pm 0.14$ | $10.7 \pm 0.9$ |
| 4 | di-$n$-Butyl ether | B | $3.61 \pm 0.23$ | $10.4 \pm 1.1$ |
| 5 | Propene | A | $3.89 \pm 0.20$ | $10.2 \pm 1.6$ |
| 6 | Propene | B | $3.96 \pm 0.18$ | $10.4 \pm 1.7$ |
| 7 | Propene | A | $3.90 \pm 0.15$ | $10.3 \pm 1.6$ |
| 8 | Propene | B | $3.98 \pm 0.20$ | $14.5 \pm 1.7$ |

[a]Irradiation light source. light-A: Xe-arc lamp + Pyrex filter, light-B: Xe-arc lamp + Pyrex filter + band-pass filter (U-340). [b]Errors quoted are two standard deviations of the calculated slopes. [c]Units: cm$^3$ molecule$^{-1}$ s$^{-1}$. Placed on an absolute basis using rate constants for the reactions of OH with cyclohexane of $(0.72 \pm 0.06) \times 10^{-11}$,[9] di-$n$-butyl ether of $(2.89 \pm 0.23) \times 10^{-11}$,[9] and propene of $(2.63 \pm 0.40) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[10] Errors quoted are two standard deviations and include the uncertainty of the reference rate constants.

The values of $k_1$ obtained from three different reference compounds and with different irradiation light sources are in good agreement with one another. The rate constant for reaction (1) can be determined to be

$$k_1 = (10.4 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

by averaging (unweighted) all sets of experiments. The error is $2\sigma$ from the average value.

**Table 2.** Summary of the rate constants for reaction of OH with isoprene

| T/K | P/kPa[a] | $k_1 \times 10^{11}$[b] | Method[c] | Referance |
|---|---|---|---|---|
| $298 \pm 2$ | 101.3 (air) | $10.4 \pm 0.4$ | RR | This work |
| 298 | 101.3 (air) | 7.4 | RR | [13] |
| 299 | 6.7, 27 (Ar) | $9.3 \pm 1.5$ | FP/RF | [14] |
| 299 | 101.3 (air) | $9.6 \pm 0.4$ | RR | [15] |
| 297 | 101.3 (air) | $10.1 \pm 0.3$ | RR | [16] |
| 298 | 0.27 (He) | $11.0 \pm 0.5$ | DF/LIF | [4] |
| 295 | 0.07–2.7 (Ar) | $7.3 \sim 9.6$[d] | LP/LIF | [5] |
| 297 | 8.0–80 (He, N$_2$, air) | $8.4 \pm 0.1$ | LP/LIF | [6] |
| 298 | 9.3–16 (N$_2$) | $10.1 \pm 0.8$ | TF/CIMS | [7] |

[a]Buffer gas. [b]Unit: cm$^3$ molecule$^{-1}$ s$^{-1}$. [c]RR: relative-rate method, FP/RF: flash photolysis/resonance fluorescence. DF/LIF: discharge flow/laser-induced fluorescence, LP/LIF: laser photolysis/laser-induced fluorescence, TF/CIMS: turbulent flow/chemical ionization mass spectrometry. [d]Pressure-dependent.

The rate constants for reaction (1) determined at near room temperature ($298 \pm 2$ K) are summarized in Table 2. The rate constant determined in this work is in agreement with the recent absolute measurements by McGivern et al.[5] and Zhang et al.[7] as well as with the relative values reported in earlier literature, with the exception of the low value reported by Cox et al.[13] The contribution of the secondary loss of isoprene by reacting with $O_3$ and O atoms was confirmed to have a negligible effect on the loss of isoprene in the present work.

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