RESEARCH ARTICLE

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Experimental kinetic study of the reactions between OH radicals and three 2-butenes over the temperature range 220–370 K and pressure range 0.67–40 kPa (5–300 Torr)

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Abstract

Gas phase reactions between OH radicals and three 2-Butenes were studied using a flash photolysis resonance-fluorescence technique over the temperature range 220-370 K and total gas pressures of 0.67 kPa (5 Torr) to 40 kPa (300 Torr). Measured rate constants exhibited weak negative temperature dependences. Most studies were carried out in argon, but some test experiments employed helium or nitrogen as the bath gas. Rate constants of OH reactions with cis-2butene and trans-2-butene were found to exhibit a pressure dependence at room temperature and above. Kinetic parameters $k_0(T)$ and $k_{\infty}(T)$ describing termolecular rate constants in Ar bath gas were derived for both reactions and can be used to calculate rate constants at the Earth's atmospheric conditions. The high-pressure limiting rate constants are $k_{\infty}^Z(T) = 5.78 \times 10^{-11} \times (\frac{298}{T})^{1.51}$, cm³ molecule⁻¹ s⁻¹ and $k_{\infty}^{E}(T) = 6.59 \times 10^{-11} \times (\frac{298}{T})^{1.54}$, cm³ molecule⁻¹ s⁻¹ for OH addition reactions with cis-2-butene and trans-2-butene, respectively. Their rate constants at 1 atm (760 Torr, 101 kPa) pressure can be represented as $k_Z(T, T)$ 1 atm) = 5.93 × 10⁻¹¹ × (T/298)^{-1.61} × exp (-17/T), cm³ molecule⁻¹ s⁻¹ and $k_E(T, T)$ 1 atm) = $6.75 \times 10^{-11} \times (T/298)^{-1.64} \times \exp(-16/T)$, cm³ molecule⁻¹ s⁻¹. The rate constant of the OH addition reaction with 2,3-dimethyl-2-butene was found to be pressure independent under our conditions and can be represented as $k_{TME}(T) =$ $14.08 \times 10^{-11} \times (T/298)^{-1.714} \times \exp(-95.7/T)$, cm³ molecule⁻¹ s⁻¹ with k_{TME} (298) K) = $(10.21 \pm 0.30) \times 10^{-11}$, cm³ molecule⁻¹ s⁻¹. Complementary measurements of IR absorption spectra of cis-2-butene and trans-2-butene were done between 500 and 3300 cm^{-1} . They are presented in Supporting Information.

K E Y W O R D S (*E*)-2-butene, (*Z*)-2-butene, 2,3-dimethyl-2-butene, hydroxyl, OH

1 | INTRODUCTION

2-Butene is an unsaturated hydrocarbon, which is used in the chemical industry. It is the simplest olefinic compound that can exist in stereo-isomeric forms, *trans*-2-butene ((E)-2-butene) and *cis*-2-butene ((Z)-2-butene). Reactions between hydroxyl radicals and 2-butenes are among the fastest OH reactions with rate constants approaching the gas kinetic collision frequency. Although a few studies of these reactions at room temperature are available, there

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are no accurate data on the temperature dependence of their rate constants near and below room temperature. Although these reactions primarily proceed via reversible addition of OH to the double bonds, there are no studies of the pressure dependence of their rates. In earlier work, we have studied OH reactions with stereo-isomers of per-fluorinated 2-butenes, cis-CF₃CF=CFCF₃ and trans-CF₃CF=CFCF₃, and found differences in their reactivities over the temperature range of atmospheric interest.¹ Presently, we use the same well-validated apparatus to accurately measure rate constants for the reactions of OH with the cis- and trans- isomers of 2-butene between 220 and 370 K, including a study of the pressure dependent behavior at total gas pressures between 0.67 kPa (5.0 Torr) and 40 kPa (300 Torr). To compare with a related larger molecule, we have also undertaken a complementary study of the reaction between OH and 2,3-dimethyl-2butene (tetramethylethylene, TME). The studied reactions are:

$$OH + (CH_3)_2 C = C(CH_3)_2 \xrightarrow{k_{TME}} Products$$
 (1)

$$OH + trans - CH_3CH = CHCH_3 \xrightarrow{\kappa_E} Products \qquad (2)$$

$$OH + cis - CH_3CH = CHCH_3 \xrightarrow{k_Z} Products$$
(3)

There are a number of relative rate studies of these reactions at room temperature between 295 and 305 K²⁻¹⁴ (seven of which are from the same research group) and three absolute rate constant measurements.^{15–17} However, only Atkinson and Pitts reported in 1975 the rate constants for Reactions (2) and (3) at three temperatures 298, 345, and 425 K. There are no other studies of rate constant temperature dependences for Reactions (1)-(3) near room temperature. There is however, a 1994 study by Sims et al.¹⁷ of Reactions (2) and (3) at extremely low temperatures (between 23 and 170 K) using a Laval nozzle. Those authors also report the room temperature rate constants measured under conventional flow conditions. The most recent study of Reactions (2) and (3) is the 2015 work of Antonov et al.,¹⁸ which covers higher temperatures of (400-800) K, but was not extended to ambient conditions.

The purpose of this study was to obtain the temperature dependences of rate constants for these three reactions around and below room temperature and to test our ability to measure accurately the rate constants of such very fast reactions. Our initial results revealed a slight dependence of the measured rate constants of reactions (2) and (3) on the bath gas pressure. This led us to conduct a more complete study of the pressure dependence to allow a more accurate prediction of the rate constants and reveal the existence of this dependence for OH addition reactions to C4 hydrocarbons near room temperature.

2 | EXPERIMENTAL DETAILS¹⁹

General descriptions of the apparatus and the experimental method used to measure the OH reaction rate constants are given in previous papers.^{20–23} Modifications to the apparatus and the measurement procedure, which resulted in significant improvements in the accuracy and precision of the obtained kinetic data, have also been extensively detailed.^{23,24}

The principal component of the flash photolysisresonance fluorescence apparatus (FP-RF) is a doublewalled Pyrex reactor (of ~180 cm³ internal volume) equipped with guartz windows. The reactor is temperature controlled by circulating liquid (ethanol or water) between the outer walls and is located in an evacuated metal housing to prevent ambient water vapor condensation during low temperature measurements. This also prevents extraneous absorption of the UV radiation from the flash lamp used to produce OH radicals. Reactions were predominantly studied in argon carrier gas at total pressures ranging between 0.67 kPa (5.0 Torr) to 40 kPa (300 Torr). A few experiments were performed in helium carrier gas over a total pressure range between 1.3 kPa (10.0 Torr) to 120 kPa (900 Torr). Due to the high efficiency of nitrogen and oxygen in quenching electronically excited OH radicals, $OH(A^2\Sigma^+)$, a resonance fluorescence detection technique does not allow accurate kinetic studies at pressures of N₂ or O₂ comparable with the He or Ar pressures used. Nevertheless, a few experiments were performed in nitrogen at 0.67 kPa (5.0 Torr). Flows of dry carrier gas, carrier gas bubbled through water thermostated at 276 K, and dilute mixtures of each reactant were passed through the reactor at total flow rates between 0.15 cm³ s⁻¹ and 4.7 cm³ s⁻¹, STP. The reactant mixtures diluted with inert gas were prepared manometrically and stored in a 10 L glass bulb equipped with Teflon/glass valves. The concentrations of the gases in the reactor were determined by measuring the gas flow rates and the total pressure with calibrated MKS Baratron manometers. Flow rates of carrier gas, the H₂O/carrier gas mixture, and the reactant/carrier gas mixture were maintained and measured using MKS mass flow controllers directly calibrated for every mixture. The calibration procedures for the mass flow controllers and manometers as well as the uncertainties associated with gas handling have been described previously.²³ The total uncertainty of the kinetic results was estimated to be ~2% to 3% in the absence of chemical complications for measurements performed after the recent modifications of the apparatus and in the measurement procedures.²³ Since the target reactions of this study are very fast, we used very dilute mixtures of reactants in the storage bulbs. Thus, most measurements were made with 0.04% mixtures of 2-butenes and a 0.008% mixture of 2,3-dimethyl-2-butene. Although the accuracy of pressure measurements when preparing mixtures did not cause any concerns, the possibility of uncontrolled adsorption/desorption of the reactant on the storage bulb walls, which could alter its concentrations and thereby affect results, need to be considered. To investigate this, test measurements were performed with mixtures of various content prepared by different methods. Thus, for 2,3-dimethyl-2-butene 0.002%, 0.0032%, 0.008%, and 0.02% mixtures were used in test experiments. For the 2-butenes, mixtures of 0.008%, 0.02%, 0.04%, and 0.08% were used in test experiments. These very diluted mixtures were prepared either in one step by diluting a pure reactant with inert gas to the required dilution or via two consecutive dilutions. No noticeable differences in the measured rate constants were observed when differently prepared mixtures were used.

Hydroxyl radicals were produced by the pulsed photolysis of H₂O, injected via the 276 K inert gas/water bubbler. The concentration of H₂O in the reactor was maintained between 5 \times 10^{14} molecule cm^{-3} and 1.5 \times 10¹⁵ molecule cm⁻³ in most measurements, while in some test experiments it varied from 1.5×10^{14} molecule cm^{-3} to 3 × 10¹⁵ molecule cm^{-3} . The OH radicals were monitored by their resonance fluorescence near 308 nm, $OH(A^{2}\Sigma^{+}) \rightarrow OH(X^{2}\Pi)$, excited by a microwave-discharge resonance lamp (≈ 0.8 kPa or ≈ 6 Torr of a mixture of H₂O in UHP helium) focused into the reactor center. Resonantly scattered radiation from the center of the reaction cell was collimated by the reactor window/lens assembly and detected by a cooled photomultiplier operating in a photon counting mode. The resonance fluorescence signal was recorded on a computer-based multichannel scaler (using a channel width of $100 \,\mu s$) as a summation of 1000 to 10,000 consecutive flashes. The entire temporal OH profile was recorded and co-added following each flash, thereby minimizing any possible effects of small flash-to-flash variations of the initial OH concentration and drift of the resonance lamp intensity.

In the absence of any reactant, the temporal decay of [OH] is associated with its net diffusion out of the irradiated (photolysis) zone. This relatively long "background" decay was always recorded with a 0.5–2.5 Hz flash repetition rate to ensure the complete disappearance of the OH between consecutive flashes. [OH] decays were then recorded at various reactant concentrations with a flash repetition rate of 1 Hz, 2.5, or 5 Hz for faster data collection except at small reactant concentrations and high pressure experiments when the low repetition rate was still



FIGURE 1 Dependence of the [OH] decay rate due to reaction with tetramethylethylene on the concentration of $(CH_3)_2C=C(CH_3)_2$ at T = 298 K and 100 Torr (13.3 kPa) pressure. A 0.008% mixture of $(CH_3)_2C=C(CH_3)_2$ in Ar from the storage bulb was used for these measurements. The relative initial concentration of OH radicals is 34%, $0.34\times[OH]_0$ (\bigstar), 100%, $[OH]_0$ (\bigoplus), and 200%, $2\times[OH]_0$ (\blacktriangledown), respectively. Concentration of water vapor (molecule cm⁻³) and flash energy (mJ) are shown in the graph. The lower panel presents residuals from the linear dependences derived by a least-square fit to the corresponding data set

required. Test experiments revealed no effect of the flash repetition rate on the measured [OH] decay rate. The procedure for deriving the OH decay rate from such data has been described by Orkin et al.^{21,23} At each temperature, the rate constant was determined from a combined fit to all of the decay rates obtained at that temperature and pressure at different reactant concentrations as illustrated in Figure 1.

2.1 | Materials

Samples of 2,3-dimethyl-2-butene, *trans*-2-butene, and *cis*-2-butene were obtained from Sigma–Aldrich Corp. with stated purities of 99.5%, 99+%, and 99.6%, respectively. Our GC/FID and GC/TCD analyses indicated sample purities of 99.3%, 99.8%, and 99.8%, respectively. The most abundant detected impurity in 2,3-dimethyl-2-butene can

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be attributed to tetramethyl oxirane (0.44%). Another smaller impurity (0.15%) could not be definitely identified by its mass spectrum and can be attributed to either 2-cyclopropyl-2-propanol or 2,3-dimethyl-3-buten-2-ol or similar unsaturated alcohol. The third impurity (0.1%) was 2,2,3-trimethyl-butane. The main impurity found in both *cis*-2-butene and *trans*-2-butene was isobutene in the amount of 0.16% and 0.18%, respectively. Another impurity (<1%) in *trans*-2-butene was not adequately resolved and identified. It could be another isomer, *cis*-2-butene, but mass-spectroscopy does not allow them to be distinguished.

Complementary to GC analysis, the possible presence of another stereo-isomer in 2-butenes was tested via IR analysis of samples, which revealed 0.55% of *cis*-isomer in the sample of *trans*-2-butene and probably $\approx 0.3\%$ of *trans*isomer in the sample of *cis*-2-butene, respectively. Detailed analysis of IR spectral data is presented in Supporting Information materials along with IR spectra of both isomers of 2-butene measured at 296 K. Therefore, the overall purity of 2-butene samples including stereo-isomer contamination was 99.27% and 99.5% for *trans*-2-butene and *cis*-2-butene, respectively.

The available samples were used without any further purification other than degassing by multiple freezepump-thaw-boil cycles. 99.9995% purity argon (*Spectra Gases Inc.*) was used as a carrier gas in almost all kinetic experiments and in the preparation of reactant mixtures. Reactants withdrawn from the liquid phase of the sample were diluted with argon in the 5 or 10 L glass storage bulbs. Thus prepared mixtures containing 0.002%–0.08% of the reactant were flowing through the reactor after pre-mixing with the main flow of Ar carrier gas and Ar + H₂O mixture. In some complementary experiments helium (99.9995% purity) and nitrogen (99.9995% purity) were used (both from Roberts Oxygen Co.) as carrier gases (see Tables 1–3).

3 | RESULTS AND DISCUSSION

3.1 | OH addition reaction rate constants measured at a constant pressure

In initial experiments, rate constants were measured between 220 and 370 K in argon at a pressure of 30 Torr (4.0 kPa) for 2-butenes and at 100 Torr (13.3 kPa) for tetramethyl ethylene. These conditions are similar to those employed by Atkinson and Pitts in the only other study of the temperature dependence for Reactions (2) and (3) near room temperature.¹⁶ Results of our measurements are presented in Tables 1–3 as bold-highlighted data and shown in Figure 2. Rate constants of all three reactions exhibit similar negative temperature dependences that can be

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FIGURE 2 Results of the rate constants measurements for OH reactions with 2,3-dimethyl-2-butene at 100 Torr of argon and with *trans*-2-butene and *cis*-2-butene at 30 Torr of argon. The solid lines show three-parameter fits to the data and the lower panels illustrate the residuals analysis for expressions (4), (5), and (6), respectively. Two standard error statistical uncertainties of individual points are hidden with symbols; they are visible in the lower panels presenting residuals plots. Dashed lines show the rate constants calculated by using expression (7) with bold-highlighted parameters $k_0(T)$ and $k_{\infty}(T)$ from Table 4 for Reactions (2) and (3), respectively (colors are swapped for better visibility)

represented with three-parameter Arrhenius expressions derived from fits to the experimental data:

 $k_{\text{TME}}(T) = 14.08 \times 10^{-11} \times (T/298)^{-1.714} \times \exp(-95.7/T) \text{ at 100 Torr}$ $k_{\text{TME}}(298K) = (10.21 \pm 0.05) \times 10^{-11}, \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{ at 100 Torr}$ (4)

 $k_{\rm E}(T) = 7.44 \times 10^{-11} \times (T/298)^{-1.87} \times \exp(-56/T) \quad \text{at 30 Torr} \\ k_{\rm E}(298K) = (6.17 \pm 0.04) \times 10^{-11}, \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at 30 Torr}$ (5)

 $k_{\rm Z}(T) = 4.49 \times 10^{-11} \times (T/298)^{-1.45} \times \exp(+54/T) \text{ at 30 Torr}$ $k_{\rm Z}(298K) = (5.38 \pm 0.04) \times 10^{-11}, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{ at 30 Torr}$ (6)

The uncertainties of k_i (298 K) are two standard errors of the fit and do not include any systematic uncertainty. Figure 2 also shows residuals from these three-parameter ROCHEMICAL KINENIOS + NO

T, K	$k_{\text{TMF}}(T) imes 10^{11}, \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$[(CH_3)_2C=C(CH_3)_2], 10^{12}$ molecule cm ⁻³	Experiment conditions ^b
220	15.28 ± 0.13	0.25-2.00	100 Torr, 0.008%
230	14.46 ± 0.08	0.24–2.52	100 Torr, 0.008%
240	13.75 ± 0.10	0.33–2.20	100 Torr, 0.008%
250	12.99 ± 0.13	0.43–2.10	100 Torr, 0.008%
260	12.41 ± 0.08	0.41-2.21	100 Torr, 0.008%
272	11.55 ± 0.12	0.58–2.50	100 Torr, 0.008%
285	10.86 ± 0.10	0.56-2.55	100 Torr, 0.008%
298	$10.15\pm0.07^{\circ}$	0.14–3.30	100 Torr, 0.008%
	10.06 ± 0.11 °	1.08–3.30	if lower concentrations excluded
	$10.01 \pm 0.04^{\circ}$	0.09–3.44	0.34×[OH] ₀
	$10.02 \pm 0.05^{\circ}$	1.05–3.44	if lower concentrations excluded
	$10.31\pm0.04^{\rm c}$	0.13–3.35	2×[OH] ₀
	$10.27 \pm 0.10^{\circ}$	1.13–3.35	if lower concentrations excluded
	10.20 ± 0.21	0.27–1.40	30 Torr, 0.008%
	10.14 ± 0.28 d	0.73–1.82	30 Torr, He , 0.002%, 0.32×[OH] ₀
	10.13 ± 0.11 ^d	0.26–1.98	300 Torr, He , 0.002%, 0.32×[OH] ₀
	10.19 ± 0.03 ^d	1.02–3.32	600 Torr, He , 0.002%, 0.7×[OH] ₀
	10.12 ± 0.11 ^d	1.04–3.08	900 Torr, He , 0.002%, 0.33×[OH] ₀
313	$\boldsymbol{9.59 \pm 0.07}$	0.34–1.66	100 Torr, 0.008%
330	$\boldsymbol{8.79 \pm 0.08}$	0.47 –3.08	100 Torr, 0.008%
350	$\boldsymbol{8.12\pm0.10}$	0.30–1.76	100 Torr, 0.008%
370	$\textbf{7.54} \pm \textbf{0.09}$	0.42–2.06	100 Torr, 0.008%
	7.64 ± 0.12	0.28–1.09	100 Torr, 0.0032%
	7.54 ± 0.10	0.36–2.08	100 Torr, 0.02%
	7.52 ± 0.20	0.20–1.82	10 Torr, 0.008%
RRSD	0.52% from the three parameter Arrhenius dependence (4)		

TABLE 1 Rate constants measured in the present work for the reaction of OH with $(CH_3)_2C=C(CH_3)_2$ (2,3-dimethyl-2-butene, tetramethylethylene)^a

^aExperiments were done using Ar as a carrier/bath gas (see footnote "d" for exceptions).

The uncertainties are two Standard Errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. They do not include any instrumental/systematic uncertainty.

The bold-highlighted values were derived from results of measurements performed at the particular temperature and 13.33 kPa (100.0 Torr) total pressure in Ar using a 0.008% mixture in the storage bulb. These data are shown in Figure 2 and were used to derive the temperature dependence (4). Other data are results of test experiments.

^b*Notes* show the total pressure, bath gas, and the reactant mixture in the storage bulb used in the measurements and test experiments. Changes in the initial OH concentration compared to the "standard" conditions ($[OH]_0$) are indicated when applicable.

^cColor highlighted data are results obtained with different initial concentrations of hydroxyl radicals (see text). The italicized values shown in the next rows were derived from the fit to the same original experimental data excluding those at the lowest reactant concentrations. The range of reactant concentrations is shown for both results.

^dResults of measurements with He as bath gas in the reactor at 298 K.

fits thus illustrating the precision of measurements. Deviation of measured values from the best fit lines can be characterized by relative residual standard deviations (RRSD),²⁴ which are smaller than 1% for all three data sets (0.52% for $k_{\text{TME}}(T)$ at 100 Torr, 0.68% for $k_E(T)$ at 30 Torr, and 0.82% for $k_Z(T)$ at 30 Torr, respectively). Such high precision (low deviation of results from the fitted temperature dependence over the entire temperature range) allowed us to conduct test experiments to check the dependence of the measured rate constants on experimental conditions. The observed weak negative temperature dependences are consistent with those available for other OH addition reactions. However, in contrast with Arrhenius dependences found for other addition reactions where the shape of the dependence was resolved, plots shown in Figure 2 are distinctively convex upwards. This seems reasonable for rate constants approaching a theoretical gas collision frequency.

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<i>Т</i> , К	$k_{ m Z}(T) imes 10^{11}, { m cm}^3$ molecule ⁻¹ s ⁻¹	[(Z)-CH ₃ CH=CHCH ₃], 10^{12} molecule cm ⁻³	Experiment conditions ^b
220	$\boldsymbol{8.84 \pm 0.10}$	0.36-2.22	30 Torr
230	8.33 ± 0.06	0.20–2.90	30 Torr
	7.96 ± 0.13	0.30–1.30	5 Torr , 0.008%
	8.20 ± 0.12	0.45-2.50	10 Torr
	8.31 ± 0.08	0.40–1.50	100 Torr, 0.008%
	7.87 ± 0.08	0.30–1.30	300 Torr , 0.008%
240	$\textbf{7.68} \pm \textbf{0.06}$	0.40-2.70	30 Torr
250	7.20 ± 0.09	0.42–2.60	30 Torr
	7.23 ± 0.03	0.42–2.50	30 Torr, 0.08%
	6.75 ± 0.06	0.53–2.40	5 Torr
	7.23 ± 0.24	0.53–2.40	10 Torr
	$\textbf{7.44} \pm \textbf{0.09}$	0.43–1.37	100 Torr , 0.008%
260	$\boldsymbol{6.62\pm0.08}$	0.50–2.98	30 Torr
272	6.32 ± 0.07	0.51–3.93	30 Torr
285	5.79 ± 0.09	0.76-3.93	30 Torr
298	5.37 ± 0.07	0.66–3.69	30 Torr
	5.40 ± 0.07	0.70–3.50	30 Torr, 0.08%
	5.08 ± 0.08	0.43-3.64	5 Torr
	5.15 ± 0.09 °	0.61–3.00	5 Torr N ₂
	5.22 ± 0.08	0.62–3.63	10 Torr
	5.47 ± 0.08	0.40-4.00	100 Torr
	5.47 ± 0.06	0.40-4.00	100 Torr, 0.08%
	5.57 ± 0.08	0.58–3.84	300 Torr , 0.008%
313	$\textbf{4.95} \pm \textbf{0.10}$	0.72-3.92	30 Torr
330	4.52 ± 0.09	0.77-4.41	30 Torr
350	$\textbf{4.16} \pm \textbf{0.07}$	1.02–4.87	30 Torr
370	$\textbf{3.80} \pm \textbf{0.05}$	0.70-5.37	30 Torr
	3.80 ± 0.07	0.70–5.04	30 Torr, 0.008%
	3.77 ± 0.06	1.02–5.00	30 Torr, 0.08%
	3.28 ± 0.14	1.10-4.60	5 Torr
	3.55 ± 0.11	1.00-4.77	10 Torr
	$\textbf{3.97} \pm \textbf{0.08}$	0.70-2.80	100 Torr , 0.008%
	$\textbf{4.02} \pm \textbf{0.03}$	0.90-5.70	300 Torr , 0.008%
	3.52 ± 0.16 °	0.79–5.00	5 Torr N ₂
	3.04 ± 0.15 °	1.00 –4.70	10 Torr He
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TABLE 2 Rate constants measured in the present work for the reaction of OH with (Z)-CH₃CH=CH-CH₃ (cis-2-butene)^a

^aExperiments were done using Ar as a carrier/bath gas (see footnote "c" for exceptions).

The uncertainties are two Standard Errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. They do not include any instrumental/systematic uncertainty.

The bold-highlighted data are results of the fit to all measurements performed at the particular temperature and pressure. These data are shown in Figures 2, 3, and 5 and were used to derive the temperature dependence (6) and parameters of the reaction rate constant presented in Table 4. Other data are results of test experiments.

^bThe total pressure in the reactor is shown. The majority of measurements were made with the reactant supplied from the glass storage bulb containing the 0.04% mixture of the reactant diluted with argon. The 0.008% and 0.08% indicate the measurements and test experiments with the corresponding mixtures in the storage bulb.

 $^{\rm c}{\rm Color}$ highlighted results of measurements with N_2 or He as bath gases in the reactor at 370 and 298 K.

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Т, К	$k_E(T) imes 10^{11},{ m cm}^3$ molecule ⁻¹ s ⁻¹	$[(E)-CH_3CH=CHCH_3],$ 10 ¹² molecule cm ⁻³	Experiment conditions ^b
220	10.12 ± 0.14	0.30–1.50	30 Torr
230	9.53 ± 0.14	0.30-2.00	30 Torr
	9.52 ± 0.14	0.30–1.36	30 Torr, 0.008%
	9.14 ± 0.21	0.20–1.37	5 Torr
	$\textbf{9.47} \pm \textbf{0.20}$	0.36-1.28	100 Torr
240	8.75 ± 0.06	0.37–2.24	30 Torr
250	8.35 ± 0.10	0.61–2.48	30 Torr
	8.20 ± 0.19	0.44–1.67	5 Torr
	8.51 ± 0.07	0.20–1.37	100 Torr
260	7.77 ± 0.14	0.60–2.48	30 Torr
272	$\textbf{7.20} \pm \textbf{0.07}$	0.42-2.70	30 Torr
285	6.64 ± 0.11	0.50–2.97	30 Torr
298	6.17 ± 0.11	0.38-3.20	30 Torr
	6.19 ± 0.09	0.22–3.62	30 Torr, 0.02%, 0.5×[OH] ₀
	6.19 ± 0.24 ^d	0.34–2.97	30 Torr, 0.02%, $[O_2] = 9 \times 10^{14}$
	5.85 ± 0.11	0.40–2.19	5 Torr
	$5.96 \pm 0.11^{\circ}$	0.90–2.89	5 Torr N ₂
	$\boldsymbol{6.08 \pm 0.15}$	0.48–1.82	10 Torr, 0.008%
	$\boldsymbol{6.30\pm0.08}$	0.53–2.09	100 Torr, 0.008%
	$\boldsymbol{6.39 \pm 0.07}$	0.60–2.21	300 Torr , 0.008%
313	5.67 ± 0.13	0.97–3.41	30 Torr
330	5.15 ± 0.09	0.77-3.71	30 Torr
350	$\textbf{4.71} \pm \textbf{0.11}$	1.02-3.95	30 Torr
370	$\textbf{4.29} \pm \textbf{0.05}$	0.70-4.42	30 Torr
	4.29 ± 0.11	1.00–3.74	30 Torr, 0.008%
	$\textbf{3.76} \pm \textbf{0.08}$	0.61–3.37	5 Torr
	$\textbf{4.10} \pm \textbf{0.17}$	1.00 –4.30	10 Torr
	$\textbf{4.50} \pm \textbf{0.04}$	0.36-2.72	100 Torr
	4.62 ± 0.06	0.47–2.65	300 Torr

TABLE 3 Rate constants measured in the present work for the reaction of OH with (*E*)-CH₃CH=CH-CH₃ (trans-2-butene)^a

^aExperiments were done using Ar as a carrier/bath gas (see footnote "c" for an exception).

The uncertainties are two Standard Errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. They do not include any instrumental/systematic uncertainty.

The bold-highlighted data are results of the fit to all measurements performed at the particular temperature and pressure. These data are shown in Figures 2, 4, 6 and were used to derive the temperature dependence (5) and parameters of the reaction rate constant presented in Table 4. Other data are results of test experiments.

^bThe total pressure in the reactor is shown. The majority of measurements were made with the reactant supplied from the glass storage bulb containing the 0.04% mixture of the reactant diluted with argon. The 0.008% and 0.02% indicate the measurements and test experiments with the corresponding mixtures in the storage bulb.

^cRed highlighted results of measurements with N₂ as bath gas in the reactor at 298 K.

^dThe result obtained with molecular oxygen added to the reactor, $[O_2] = 9 \times 10^{14}$ molecule cm⁻³, which exceeds the leak from the atmosphere by three orders of magnitude.

3.2 | Studying very fast reactions

3.2.1 | Tetramethyl ethylene, $(CH_3)_2C=C(CH_3)_2$

There are two possible kinetic complications, which can result in overestimating the OH reaction rate constant determined in FP-RF experiments: (i) secondary reactions of OH with a radical product of the reaction under study or (ii) reactions of OH with possible radical products formed by photolysis of the reactant.²² Even small amounts of such radicals of either photolytic or reactive origin can increase measured OH decay rates if they are substantially more reactive than the target reactant. We have previously

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observed the influence of the reactant photolysis products on measured OH reaction rate constants in a number of studies,^{22,25-27} whereas a small effect of OH reaction with reaction products could occasionally be observed only at intentionally increased initial OH concentrations.²⁴ Both complications should become negligible when the rate constant of the target reaction approaches a collision frequency as in the case of the reactions studied here. All three compounds studied in this work are very strong absorbers in the UV region below 200 nm.²⁸ Their absorbance is comparable with that of *cis*-CHCl=CHCF₃, carefully studied earlier, where photolysis of the reactant resulted in a 1.5%-4.5% overestimation of the measured rate constant.²⁵ However, the reactant concentrations used in the current study are at least two orders of magnitude smaller than in the abovementioned work. Thus, a much smaller possible amount of photolysis products, which also cannot react with OH substantially faster than the target compound, makes the contribution of such process vanishingly small. The formation of radical products in the reaction under study never caused a noticeable problem in our previous measurements. It cannot be a problem in this study simply because such secondary reactions cannot be substantially faster than the target reactions. Nevertheless, test experiments were done with variations of both initial OH concentration and flash energy. No substantial changes in the measured rate constants were observed.

As mentioned earlier, all three reactions are very fast and, therefore, relatively low concentrations of reactants were used in this study. Although the molecular reactant (2-butene) is always in excess over OH, this raises a concern on the possibility of the small yet noticeable consumption of the reactant due to reactions with OH radicals if their concentrations become comparable. Such reactant consumption could affect the measured OH decay rates by decreasing the reactant concentration, which can be most pronounced at the lowest reactant concentrations. Any effect should also depend on the initial OH concentration and could be most pronounced in the case of the fastest Reaction (1), where the lowest reactant concentrations were used. Two types of data suggest that the reported rate constants are not affected noticeably by this potential complication. Both are illustrated here with the data obtained at 298 K and 100 Torr (see Figure 1 and the first six lines at 298 K in Table 1). Firstly, the test experiments with either higher or lower initial [OH] yielded almost negligible effect on the measured rate constant, $k_{\text{TME}}(298)$ K). Figure 1 presents dependences of measured [OH] decay rates due to reaction with $(CH_3)_2C=C(CH_3)_2$ on the concentration of the reactant at three different initial concentrations of hydroxyl radicals. Black circles represent the data obtained with $[H_2O] \approx 1.6 \times 10^{15}$ molecule cm⁻³ in

the reactor and an electric discharge energy of ≈ 25 mJ per flash whereas green upward pointing triangles represent data obtained with the same flash energy and $[H_2O] \approx 0.55$ \times 10¹⁵ molecule cm⁻³, that is, with an initial OH concentration that is almost three times smaller. Typical rate constant measurements were made using OH concentrations between these two values. Red downward pointing triangles represent data obtained with $[H_2O] \approx 1.6 \times 10^{15}$ molecule cm^{-3} and flash energy of ≈ 50 mJ, that is, with the initial OH concentration that is a factor of two larger than in our measurements. The lower panel of Figure 1 presents residuals from the least-squares fits of a linear dependence to the corresponding data sets to illustrate their quality. The rate constants, k_{TME} (298 K), derived from these data are presented in Table 1 highlighted with the corresponding colors. Although the rate constant values derived from these experiments can be distinguished, the difference between them is very small. Secondly, we reanalyzed these three series of data but using only higher reactant concentrations from each experiment, that is, we removed the most suspicious data obtained at the lowest reactant concentrations from each series before the fit. The rate constants obtained under the restricted reactant concentration ranges are presented in the italics. One can see that although the lowest concentrations in the series became an order of magnitude larger, the derived rate constants, k_{TMB} (298 K), are statistically indistinguishable. Similar analysis over the different range of reactant concentration was done for the data obtained at other temperatures. Therefore, we can conclude that the rate constants measured in the present work are not affected by this complication.

Test experiments were also done to check the stability of a diluted mixture used to measure $k_{\rm TMB}({\rm T})$. Results obtained with a freshly prepared 0.008% mixture are indistinguishable from those obtained with the same mixture two months later, that is, the difference is less than the uncertainty of any of the two values. The long-term reproducibility of our measurements was checked in test experiments 4 years later in a different reactor, with a modified gas handling system, and all new calibrations of flow controllers. $k_{\rm TMB}({\rm T})$ values obtained between 230 and 330 K differ from those measured 4 years before by 1%–1.5%. Similar test measurements at room temperature resulted in $k_{\rm Z}(298~{\rm K})$ and $k_{\rm E}(298~{\rm K})$ values, which differ from previously measured ones by less than 1.5%.

3.2.2 | Effect of reactive impurities

Possible reactions between OH and impurities in the samples of target reactants is another common prob-

lem of absolute rate constant measurements. Even small amounts of impurity can affect the results if the impurity reacts with OH much faster than the target compound. However, this is not the case of very fast reactions studied in this work because impurities cannot react much faster than the reactant under study. Although there is no OH reactivity information for all identified impurities in the samples only unsaturated compounds could have comparable reactivity.

The most abundant impurity (0.44%) in tetramethyl ethylene (TME, $(CH_3)_2C=C(CH_3)_2$) is probably tetramethyl oxirane, which can be a product of TME oxidation. Although there are no data on OH reactivity of this chemical, we can consider similar molecules. 2,3-dimethylbutane also have four reactive -CH₃ groups and its room temperature OH reaction rate constant is ≈ 6 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.²⁹ Methyl oxirane (propylene oxide) has only one -CH₃ group and its room temperature OH reaction rate constant is \approx (3-5) \times 10⁻¹³ cm³ molecule⁻¹ s⁻¹.³⁰ Thus we can suggest that the OH reaction rate constant of tetramethyl oxirane does not exceed $(2-6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, that is, substantially smaller than k_{TME} (298 K) and the presence of this impurity (0.44%) results in slight underestimation (less than 0.4%) of $k_{\text{TME}}(T)$ derived in our study, unless the TME concentration is corrected. Another major detected impurity (0.15%) can be either saturated 2-cyclopropyl-2-propanol or unsaturated 2,3-dimethyl-3-buten-2-ol alcohol. The first one is a saturated compound and its OH reactivity is expected to be similar to that of tert-butanol, (CH₃)₃COH, whose room temperature OH reaction rate constant is only $\approx 1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹,³⁰ that is, two orders of magnitude smaller than $k_{\text{TME}}(298 \text{ K})$ measured here. The second one is unsaturated compound with the $=CH_2$ group and its reactivity toward OH is expected to be similar to that of isobutene, $CH_2 = C(CH_3)_2$, whose OH reaction rate constant at room temperature is $\approx 50\%$ of $k_{\text{TME}}(298)$ K).³⁰ Thus, the presence of the second major impurity can result in only a small error (<0.15%) of the measured k_{TME} . The third one, 2,2,3-trimethyl-butane, (0.1%) reacts with OH with the rate constant of $\approx 4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹³⁰ and thus cannot contribute to the measured $k_{\text{TME}}(T)$

In the course of this study, we also had a very old sample of TME, $(CH_3)_2C=C(CH_3)_2$, with much larger amount of these two major impurities of about 13% each (GC-TCD data) along with numerous smaller impurities. The OH reaction rate constant obtained with this contaminated sample (with no correction of the TME concentration for the impurity presence) was $\approx 17\%$ smaller than $k_{TME}(T)$ at both 298 and 370 K reported in Table 1. These "complementary" measurements are indicative that both impurities are less reactive toward OH than the target compound,

 $(CH_3)_2C=C(CH_3)_2$. Therefore, their presence in the total detected amount of 0.59% may result in underestimating the measured $k_{TME}(T)$ by less than $\approx 0.6\%$ unless the TME concentration is corrected.

Both stereo-isomers of 2-butene exhibit similar OH reactivity and small detected inter-contamination cannot affect our results. Another impurity found in both isomers was isobutene, $CH_2=C(CH_3)_2$, whose OH reactivity³⁰ is similar to that of *cis*-2-butene. The presence of detected impurities can result in underestimating the measured values of k_E and k_Z by less than 0.1%. Thus, we can conclude that the presence of impurities in the samples does not affect our results of rate constants measurements for all OH title reactions, k_{TME} , k_Z , and k_E .

3.3 | Pressure dependence study

3.3.1
$$\mid$$
 (CH₃)₂C=C(CH₃)₂

Reaction (1) has also been studied at T = 298 K in helium carrier gas between 30 Torr (4.0 kPa) to 900 Torr (120 kPa) to find no pressure dependence of the measured rate constant. The results obtained at the highest temperature of T = 370 K in 10 Torr and 100 Torr (4.0 and 13.3 kPa) of argon are statistically indistinguishable within the combined uncertainties. The use of various mixtures of reactant in the storage bulb ranging between 0.002% and 0.02% revealed no difference in the measured rate constants thus supporting our confidence in the correct reactant concentration when a 0.008% mixture was used to obtain the bold highlighted data and derive the Arrhenius expression (4) for the reaction rate constant $k_{\text{TME}}(T)$.

3.3.2 | $CH_3CH = CHCH_3$

Reactions (2) and (3) have been studied between 5 Torr and 300 Torr in argon bath gas at T = 298 K and T = 370 K to reveal a noticeable dependence of the measured rate constants on pressure (see Figures 3 and 4). Although results obtained at lower temperatures, T = 250 K and T = 230 K, are also indicative of a pressure dependence, it is not as pronounced as at the higher temperatures. Thus, both these association reactions are still in the fall-off region and did not achieve the high-pressure limit at room temperature and above.

In addition to the test experiments with different reactant mixtures in the storage bulb and variation of initial hydroxyl concentrations in the reactor, $[OH]_0$, other specific test experiments were performed with the 2-butenes. The rate constant was measured in the presence of molecular oxygen added to the reactor with the carrier gas to

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FIGURE 3 Results of measurements of the rate constant for the reaction between OH and *cis*-2-butene at various pressures of argon carrier gas at temperatures of 230, 250, 298, and 370 K (solid circles). Also shown are results obtained at 10 Torr of helium (green open circle at 370 K) and at 5 Torr of nitrogen (red open squares at 370 and 298 K) as carrier gases. Dashed lines show the fits of expression (7) to the data obtained at 298 and 370 K, which yielded both parameters $k_0(T)$ and $k_{\infty}(T)$; they were used to calculate dependences shown for 250 and 230 K. Solid lines show the dependences calculated with expression (7) and the bold-highlighted parameter $k_{\infty}(T)$ from Table 4 (see text for explanations)

check its possible effect on the observed kinetics of OH. The concentration of oxygen, $[O_2]$, in these experiments was at least three orders of magnitude larger than it could be expected due to stated oxygen impurities in the carrier gas or the measured leak from the atmosphere at any pressure and the total carrier gas flow rate in our experiments. The rate constants measured in the presence of oxygen were indistinguishable from those obtained without added oxygen thus suggesting that the possible small impurities of oxygen do not affect the results of our measurements.

We used the fall-off expression for termolecular reactions adopted by NASA Data Panel³¹ to describe the rate constants obtained at T = 370 K and T = 298 K in Ar,

$$k([M],T) = \left(\frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_{\infty}(T)}}\right) \times 0.6^{\left\{1 + \left[\log_{10}\left(\frac{k_0(T)[M]}{k_{\infty}(T)}\right)\right]^2\right\}^{-1}}$$
(7)

where the temperature dependences of low-pressure and high-pressure limiting rate constants are represented as

$$k_0(T) = k_0^{298} \left(\frac{298}{T}\right)^n$$
 and $k_\infty(T) = k_\infty^{298} \left(\frac{298}{T}\right)^m$, respectively. (8)



FIGURE 4 Results of measurements of the rate constant for the reaction between OH and *trans*-2-butene at various pressures of argon carrier gas at temperatures of 230, 250, 298, and 370 K. Also shown are results obtained at 5 Torr of nitrogen (red open square at 298 K) as carrier gas. Dashed lines show the fits of expression (7) to the data obtained at 298 and 370 K, which yielded both parameters $k_0(T)$ and $k_{\infty}(T)$; they were used to calculate dependences shown for 250 and 230 K. Solid lines show the dependences calculated with expression (7) and the bold-highlighted parameter $k_{\infty}(T)$ from Table 4 (see text for explanations)

Thus, parameters k_0^{298} , k_∞^{298} , k_0^{370} , and k_∞^{370} were derived from the fit of expression (7) to the data obtained at 298 and 370 K, respectively, and parameters *n* and *m* were then calculated. These parameters are presented in Table 4 (italicized second line for each compound). Expression (7) with these parameters has been used to calculate pressure dependences for both rate constants, $k_E(P, T)$ and $k_Z(P, T)$, at all four temperatures, 370, 298, 250, and 230 K. Results are shown with dashed lines in Figures 3 and 4. These dependences describe the data series quite well at 298 and 370 K, from which they have been derived. However, they systematically underestimate the rate constants measured at lower temperatures of 250 and 230 K by a slight amount 2%–6%.

Although rate constants $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ exhibit some pressure dependence, both are very close to their highpressure limits, and, therefore, values of $k_0(T)$ derived from the fit may have large uncertainties. They do contribute to the observed pressure dependences at lower pressures at 298 and 370 K. However, the high-pressure limiting rate constant, $k_{\infty}(T)$, is the main contributor to the reaction rate constant values especially at lower temperatures and higher pressures. In another approach to describing these data, we have accepted the same TABLE 4 Rate constants for termolecular reactions between OH and 2-butenes in Ar bath gas^a

Molecule	$k_0^{298} imes 10^{26}, m cm^6$ molecule ⁻² s ⁻¹	n	$k_{\infty}^{298} imes 10^{11}, { m cm}^3$ molecule ⁻¹ s ⁻¹	m	<i>k</i> (298 K, 760 Torr), cm ³ molecule ⁻¹ s ⁻¹	
(Z)-CH ₃ CH=CHCH ₃	$\pmb{2.81 \pm 0.52}$	7.46	5.78 ± 0.04 °	1.51 °	$\textbf{5.61} \times \textbf{10}^{-\ 11}$	
			5.74 ± 0.04^{b}	1.39 ^b	5.58×10^{-11}	
(E)-CH ₃ CH=CHCH ₃	3.59 ± 1.21	7.65	6.59 ± 0.03 °	1.54 °	$\textbf{6.40}\times\textbf{10}^{-11}$	
			6.60 ± 0.06^{b}	1.44 ^b	6.42×10^{-11}	
$(CH_3)_2C = C(CH_3)_2$			10.21 ± 0.05		10.21×10^{-11}	
	$k_{\text{TME}}(T) = 14.08 \times 10^{-11} \times (\text{T}/298)^{-1.714} \times \exp(-95.7/\text{T})^{\text{d}}$					

^aParameters, k_0^{298} , n, k_{∞}^{298} , and m, were derived from the fit of expressions (7) and (8) to the experimental data by using two approaches.^{b,c} The uncertainties are two Standard Errors from the least-squares fits. They do not include any instrumental/systematic uncertainty. Bold highlighted data are preferred results. The total uncertainty of $\approx 3\%$ (T = 230-370 K) is estimated as a sum of two standard errors from the fit and an estimated instrumental/systematic uncertainty. ^bAll four parameters, k_0^{298} , n, k_{∞}^{298} , and m, were derived from the fit to the experimental data obtained at 298 and 370 K only.

^cParameters, k_0^{298} and *n*, were derived from the fit to the experimental data obtained at 298 and 370 K. Then, parameters k_{∞}^{298} and m were derived from the fit to all data obtained at 30 Torr over the entire temperature range.

^dExpression was derived from the fit to the experimental data obtained at 100 Torr. The rate constant was found to be pressure independent below 370 K.

low-pressure limiting rate constant, $k_0(T) = k_0^{298} (\frac{298}{T})^n$, that is, parameters k_0^{298} and *n*, derived from the pressure dependences obtained at 298 and 370 K where they are most pronounced. However, parameters for the highpressure limiting rate constants, $k_{\infty}(T)$ and *m*, have been derived from the fit of expression (7) to the more representative data set obtained at 30 Torr, which is shown in Figure 2 and listed as bold-highlighted values in Tables 2 and 3. Thus derived values of $k_{\infty}(T)$ and *m* are bold-highlighted in Table 4 and yield the following high-pressure limiting rate constants for Reactions (2) and (3), respectively to be used below room temperature

$$k_{\infty}^{Z}(T) = 5.78 \times 10^{-11} \times \left(\frac{298}{T}\right)^{1.51}$$
 (9)

$$k_{\infty}^{E}(T) = 6.59 \times 10^{-11} \times \left(\frac{298}{T}\right)^{1.54}$$
 (10)

Pressure dependences calculated with these parameters at 370, 298, 250, and 230 K are shown in Figures 3 and 4 with solid lines. These calculated dependences adequately describe below room temperature data but underestimate those obtained at 370 K by $\approx 2\%$. Representing either $k_0(T)$ or $k_{\infty}(T)$ with Arrhenius temperature dependence did not improve the quality of the fitting. Dashed lines are added in Figure 2 to show rate constants $k_E(T)$ and $k_Z(T)$ calculated at 30 Torr by using expression (7) with boldhighlighted parameters from Table 4 (colors are swapped for better visibility). Note, that values of $k_{\infty}(T)$ derived by using both approaches coincide within their statistical uncertainty.

The pressure independent bimolecular H-abstraction reactions can contribute to reactions of both isomers of 2-butenes at higher temperatures

$$OH + CH_3CH = CHCH_3 \xrightarrow{k_{11}} H_2O + CH_3CH = CH\dot{C}H_2$$
(11)
$$OH + CH_3CH = CHCH_3 \xrightarrow{k_{12}} H_2O + CH_3CH = \dot{C}CH_3$$
(12)

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along with termolecular addition reactions that we are trying to describe with expression (7). Antonov et al.¹⁸ concluded that H-abstraction reactions can contribute significantly only above 650-700 K. These researchers found that H-abstraction from a methyl group, Reaction (11), was the fastest H-abstraction channel in the reaction between OH and 2-butenes based on their kinetic analysis of experimental data obtained at higher temperatures (above 400 K) and a theoretical study of reaction channels. Based on their results, $k_{11}(370 \text{ K})$ can be estimated as $\approx 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $\approx\!\!2\times10^{-13}~cm^3$ molecule^{-1} s^{-1} for trans-2-butene and cis-2-butene, respectively at the highest temperature of our study,¹⁸ thus contributing less than 0.7% and 0.5%, respectively to the total measured OH reaction rate constant at this temperature. The contribution becomes less than 0.2% and 0.1%, respectively at 298 K. There are theoretical estimations suggesting that H-abstraction from olefinic C-H group is slow and thus cannot contribute to $k_E(T)$ and $k_Z(T)$ values measured below 370 K.^{18,32,33} Thus $k_E(T)$ and $k_Z(T)$ characterize the termolecular addition of OH to 2-butenes. However, H atom abstraction could potentially affect the derived parameters $k_0(T)$ and $k_{\infty}(T)$ and limit the validity of extrapolations beyond our measurement conditions.

3.3.3 | Relative efficiencies of Ar, He, and N_2 as the third body

The termolecular nature of Reactions (2) and (3) was revealed from kinetic measurements at different pres-

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sures of Ar carrier gas. Test experiments with different bath/carrier gasses were also done to qualitatively support this finding. Reaction (3) between OH and cis-2-butene has been studied at T = 370 K using He and N₂ as carrier gases at 10 Torr and 5 Torr, respectively. The measured rate constants are noticeably different from those measured in Ar bath gas at the same pressure, being $\approx 17\%$ smaller in He and $\approx 7\%$ larger in N₂, respectively. The results are shown in Figure 3 with red and green symbols, respectively and highlighted with the same colors in Table 2. These results further demonstrate the termolecular nature of the reaction, with He being less efficient and N₂ being more efficient than Ar as a third body. These experiments were done at highest temperature and lowest pressures where the effect of the third body nature is expected to be most pronounced. Additional test experiments with nitrogen as a carrier gas were done at 298 K and 5 Torr of N₂ for both isomers. Rate constants $k_Z(298 \text{ K})$ and $k_E(298 \text{ K})$ appear barely larger than the corresponding values measured in Ar carrier gas at 5 Torr with their uncertainties still overlapping (see red symbols in Figures 3 and 4 and red highlighted data in Tables 2 and 3). The effect of nitrogen is noticeably smaller than it was at 370 K.

Although these tests were rather qualitative we can roughly estimate the low-pressure limiting rate constant for these bath gases at 370 K, k_0^Z (370 K), from expression (7) and already derived k_{∞}^Z (370 K). It is 1.8×10^{-27} for helium and 10×10^{-27} for nitrogen compared to 5.6 $\times 10^{-27}$ for argon as derived in our study (units are cm⁶ molecule⁻² s^{-1}). Note, that even at these conditions, 5 Torr and 370 K, measured rate constants are close to the high-pressure limiting value for this reaction and, therefore, thus obtained values of k_0^Z (370 K) should be considered as rough estimates. Nevertheless, we can make some clarifications of these values. All further estimations are based on validity of expression (7), which describes pressure dependence of a termolecular reaction. We can use this expression to calculate uncertainties of k_0^Z (370 K) for all three gases based on uncertainties of k_Z (370 K) measured at 5 Torr (Ar and N₂) and 10 Torr (He) reported in Table 2 combined with the uncertanty of k_{∞}^{Z} (370 K). These calculations result in k_{0}^{Z} (370 K) equals to $(1.8_{-0.4}^{+0.6}) \times 10^{-27}$ for helium, $(5.6_{-1.4}^{+2.3}) \times 10^{-27}$ for argon, and $(10.3_{-3.6}^{+8.2}) \times 10^{-27}$ for nitrogen (units are cm⁶ molecule⁻² s⁻¹). Relatively large uncertainties were expected because all rate constants are close to the high-pressure limiting value, k_{∞}^Z (370 K). As one could expect, although uncertainties of the measured values of k_Z (370 K) are similar, the relative uncertainty of calculated k_0^Z (370 K) increases as the rate constant gets closer to the high-pressure limiting value in the series He–Ar– N_2 .

Assuming the same relative efficiency of nitrogen as the third body at 298 K, we can calculate $k_Z(298 \text{ K})$ at 5 Torr of N₂ to be \approx (5.21 ± 0.1) × 10⁻¹¹ cm³ molecule⁻¹ s^{-1} . The uncertainty was derived by calculating k_7 (298 K) from expression (7) by using the highest and lowest values of k_0^Z (370 K) in N₂ estimated above. Thus calculated value is 0.7% to 4.6% larger than $k_Z(298 \text{ K})$ measured at 5 Torr of Ar. The upper limit of the difference, 4.6%, would be relatively easily detectable in our experiments. However, the results of test experiments under these conditions (see Table 2) are rather suggestive of the lower-side difference within the uncertainty interval since values measured in argon and nitrogen bath gases coincide within their combined uncertainties. The similarity of cis-2-butene and trans-2-butene molecules and the pressure dependences of their OH reaction rate constants suggest a similar effect of different bath gases on both reactions. Indeed, $k_{\rm E}(298$ K) values measured at 5 Torr of Ar and N₂ also almost coincide within their uncertainties (see Table 3). The calculated difference becomes even smaller at higher pressures and, thus, there is no way to detect it from the experiment. Values of $k_Z(298 \text{ K})$ and $k_E(298 \text{ K})$ calculated at 1 atm (760 Torr) of nitrogen are only $\approx 0.3\%$ larger than in argon.

3.3.4 $+ k_Z(T)$ and $k_E(T)$ at atmospheric conditions

Reaction (1) was studied over the temperature range of atmospheric conditions to be pressure independent. Although our study of the pressure dependence of OH addition to 2-Butenes, Reactions (2) and (3), was done using Ar as the bath gas, thus determined OH reaction rate constants can be used under conditions existing in the Earth's troposphere. Firstly, both $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ calculated at 1 atm (760 Torr) of Ar are already at $\approx 97\%$ of their high-pressure limiting values at 298 K. Secondly, the test measurements supported by calculations indicated very small difference between rate constants in Ar and N₂ bath gases at T = 298 K and 5 Torr pressure. The calculated difference becomes even more negligible at higher pressures and the lower temperatures relevant to the troposphere.

Thus, the rate constants calculated by using expressions (7) and (8) with parameters from Table 4 can be used to describe Reactions (2) and (3) in the Earth's troposphere. The rate constants, $k_Z(T_h, P_h)$ and $k_E(T_h, P_h)$ calculated for different altitudes (different pressures, P_h , and corresponding temperatures, T_h) from the bottom of the troposphere through the tropopause are within 1% of those calculated at 1 atm (760 Torr). These rate constants, $k_Z(T_h, 1 \text{ atm})$ and $k_E(T_h, 1 \text{ atm})$, are shown in Figures 5 and 6 with long-dashed red lines. They can be represented by the following expressions derived from the fit to the rate constants cal-

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culated at 1 atm (760 Torr pressure) between 400 and 160 K by using expressions (7) and (8) with bold highlighted parameters from Table 4.

$$k_{\rm Z}(T, 1 \text{ atm}) = 5.93 \times 10^{-11} \times (T/298)^{-1.61}$$
$$\times \exp(-17/T), \text{ cm}^3 \text{molecule}^{-1}\text{s}^{-1} (13)$$
$$k_{\rm E}(T, 1 \text{ atm}) = 6.75 \times 10^{-11} \times (T/298)^{-1.64}$$
$$\times \exp(-16/T) \text{ cm}^3 \text{molecule}^{-1}\text{s}^{-1} (14)$$

Although all three expressions, (4), (13), and (14) for $k_{\text{TME}}(T)$, $k_Z(T)$, and $k_E(T)$, may have limited usage above ≈ 400 K because of the termolecular nature of reactions and the limited temperature range of our measurements, they accurately characterize Reactions (1)–(3) at atmospheric conditions.



FIGURE 6 Available results of temperature dependence studies for the reaction between OH and *trans*-2-butene. ——this study (30 Torr, Ar); O— Atkinson & Pitts¹⁶ (50 Torr, Ar); . \bigcirc —Sims et al.¹⁷ (14 Torr, Ar); \bigtriangledown —Antonov et al.¹⁸ (2-4 atm, He) and \triangle —Antonov et al.¹⁸ (1-2 atm, He); ——calculated based on our results for experimental conditions of Antonov et al.'s.¹⁸ Error bars of Antonov et al.¹⁸ represent one standard error whereas those of Sims et al.¹⁷ are 95% confidence intervals and the total uncertainty reported by Atkinson & Pitts¹⁶ also include estimated systematic uncertainties. _____ Three parameter fit to our data obtained at 30 Torr (expression (5)) and ______ its extrapolation beyond the temperature range of our study; _____ calculated rate constant at 30 Torr, $k_Z(T, 30 Torr)$; _____ calculated $k_{\infty}^E(T)$

3.4 | Comparison with the available data

3.4.1 | Room temperature measurements

Table 5 summarizes the available data at room temperature. The left part of the table shows the available results of absolute rate constant measurements slightly corrected by using the temperature dependences derived in our work to recalculate the values at T = 298 K. The results of relative rate measurements are shown in the right part as they are reported at temperatures between 295 and 305 K. The uncertainties of relative rate measurements are not shown because they are mainly due to uncertainties of the reference reactions. The first column presents results of our work calculated at 298 K and 1 atmosphere from Table 4 with the total estimated uncertainty.

There is good agreement between our result for Reaction (1) and those from relative rate studies^{2-4,6-8} performed by two different research groups at atmospheric pres-

TABLE 5 Room temperature reaction rate constants determined in this study and available in the literature (units are 10^{-11} cm³ molecule⁻¹ s⁻¹)

This study ^a $T = 298 K$	Absolute mea	surements ^b T =	= 298 K	Relativ	e rate m	easurem	ents ^c $T =$	295-305	К	
$OH + cis-CH_3CH = CHCH_3$										
$\textbf{5.61} \pm \textbf{0.14}$	5.35 ± 0.54^{16}	4.26 ± 0.25^{15}	6.08 ± 0.56^{17}	6.51 ¹²	6.18 ¹³	5.60 ⁴			5.48 ⁸	8.9 ⁹
$OH + trans-CH_3CH = CHCH_3$										
$\textbf{6.40} \pm \textbf{0.19}$	7.07 ± 0.70^{16}		6.71 ± 0.22^{17}	10.6 ¹⁴	7.21 ⁵	6.39 ⁴	6.09 ¹⁰	7.31 ¹¹		10.9
$\mathbf{OH} + (\mathbf{CH}_3)_2 \mathbf{C} = \mathbf{C}(\mathbf{CH}_3)_2$										
10.21 ± 0.30		5.69 ± 0.13^{15}		10.8 ²	10.9 ³	11.0 ⁴	11.1 ⁶	10.87	10.3 ⁸	22. ⁹

^aRate constants derived in this study are calculated for T = 298 K and pressure of 1 atmosphere of argon bath gas. Listed total uncertainties include two Standard Errors from the least-squares fits and estimated instrumental uncertainty.

^bRate constants reported in [17] were measured at 295 K. They have been slightly corrected to find the value at 298 K by using the temperature dependences derived in our study.

Although all absolute measurements were performed at below one atmosphere pressures (14 Torr $(Ar)^{17}$; 20 Torr $(He)^{15}$ and 3 Torr $(He)^{15}$; 50 Torr $(Ar)^{16}$), neither one revealed the pressure dependence of the measured rate constant.

^cResults of almost all relative rate studies were obtained at \approx 1 atmosphere between 295 and 305 K and presented with no adjustment to 298 K. Such adjustment should account for the similar temperature dependences of reference reactions, thus offsetting the correction to some extent making it negligible. The relative rate study [9] was done at \approx 1 Torr (He) by using a discharge flow technique. We calculated rate constants by using the reported relative rates and the currently recommended rate constant for the reference reaction, OH + CH₂ = CHCH₃.³¹

We do not show the uncertainties of these results because they can be mainly due to uncertainty of the reference reactions.

sure. Results from these the same groups are also in good agreement with our data for two other Reactions (2)^{4,10} and (3).^{4,8} Rate constant ratios measured at low pressure of \approx 1 Torr (He) in discharge flow experiments reported in 1971⁹ were recalculated by using the currently recommended rate constant of the reference reaction, OH + CH₂=CHCH₃,³¹ and noticeably exceed other results for all three reactions.

3.4.2 | Temperature dependence studies

To the best of our knowledge, there is no study of the temperature dependence of the OH reaction rate with tetramethyl ethylene (1), $k_{\text{TMF}}(T)$. There are three absolute measurements of OH reaction rate constants with both stereo-isomers of 2-butene, $k_E(T)$ and $k_Z(T)$, over non-overlapping temperature intervals. All temperature dependent data reported between 170 and 800 K are shown in Figures 5 and 6 along with results derived in our work. These figures present data points obtained in our work at 30 Torr (similar to Figure 2 with bold highlighted data from Tables 2 and 3) and the corresponding threeparameter Arrhenius dependences, expressions (5) and (6), respectively, derived from fits to these data. These temperature dependences are shown with solid blue lines (over the temperature range of measurements) and extrapolated beyond the temperature range of experiments with dashed blue lines in both figures. On the other hand, our measurements revealed a pressure dependence of the rate constants $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ thus suggesting a fall-off regime of these association Reactions (2) and (3) especially at higher temperatures. Therefore, their rate constants

should be calculated using theoretical expression (7) with parameters $k_0(T)$ and $k_{\infty}(T)$ derived from our data and presented in Table 4. This is especially important if we are going to estimate $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ at temperatures exceeding the temperature range over which they have been measured. Figures 5 and 6 show calculated $k_{\infty}(T)$ values with solid red lines. Rate constants $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ calculated at 30 Torr pressure are also shown with short-dashed red lines. They can be compared with simple extrapolations of three-parameter Arrhenius dependences (5) and (6), which are drawn through the data obtained at 30 Torr (dashed blue lines) to see the substantial divergence at higher temperatures beyond the range of measurements. The long-dashed red lines in Figures 5 and 6 show the rate constants $k_E(T)$ and $k_Z(T)$ calculated at 760 Torr (1 atm) pressure.

Atkinson and Pitts¹⁶ measured rate constants for reactions of both isomers of 2-Butene, $k_Z(T)$ and $k_E(T)$, at 298, 346, and 425 K by using a FP-RF technique. All measurements were done at 50 Torr of argon. There is very good agreement between their results for $k_Z(T)$ and those measured and calculated in our work whereas their reported values for $k_E(T)$ are 10%–20% higher. Sims et al.¹⁷ studied both reactions at very low temperatures employing a Laval nozzle. They also reported room temperature rate constants measured using conventional LIF at 14 Torr of argon, which exceed our results by $\approx 10\%$. The extrapolation of the temperature dependences derived from our data are in good agreement with their results obtained at 170 K, the highest temperature of their measurements at verylow temperatures (see Figures 5 and 6), being 9% larger in case of $k_{\rm E}$ (170 K) and 2% smaller in case of $k_{\rm Z}$ (170 K). Their temperature dependences flatten out at lower temperatures of 75, 44, and 23 K for both reactions and are not shown.

In the most recent study, Antonov et al.¹⁸ obtained rate constants of both isomers of 2-Butene between 400 and 800 K at higher pressures of helium ranging between 1 Bar to 20 Bar. Laser pulse photolysis of acetylacetone was used to produce OH radicals, which were detected by LIF. Rate constants for OH addition, $k_E(T)$ and $k_Z(T)$, were derived from a kinetic analysis of pronounced nonsingle-exponential decays of the OH concentration by applying a multi-channel mechanism of OH addition to 2-butene.¹⁸ Rate constants for abstraction of the methyl hydrogens, $k_{11}(T)$, were also derived in this analysis to be much smaller than $k_E(T)$ and $k_Z(T)$ at below 500 K. All their reported data for the addition channels, $k_Z(T)$ and $k_E(T)$, are shown with triangles in Figures 5 and 6. Similar to the authors' presentation,¹⁸ the error bars are one standard error, which makes Figure 6 more readable. Downward pointing triangles in both Figures 5 and 6 show rate constants determined from measurements at pressures of 2 Bar to 4 Bar. Antonov et al.¹⁸ claim these rate constants are at their high-pressure limit, which is supported by results of test experiments at pressures up to 20 Bar. These "high-pressure" results for the addition reaction of trans-2-butene (shown in Figure 6 with downward pointing triangles) are consistent with our prediction for these higher temperatures although the data of Antonov et al.¹⁸ have large uncertainties and exhibit large scattering. In contrast, their more limited data for the reaction of cis-2-butene (shown in Figure 5) demonstrate a very different temperature dependence although the reported uncertainties are too large to allow a definitive conclusion. We calculated $k_{\rm E}(T)$ and $k_{\rm Z}(T)$ for all temperatures and pressures reported by Antonov et al.,¹⁸ that is, for all their data presented in Figures 5 and 6 by using expression (7) with parameters $k_0(T)$ and $k_{\infty}(T)$ from Table 4. The thusly calculated data are shown with grey circles for both reactions.

Results of a few complementary measurements of $k_E(T)$ reported by these authors at three temperatures are of particular interest. Rate constants have been measured at two different pressures at each temperature: 650 K (3 Bar and 1 Bar), 675 K (4 Bar and 2 Bar), and 700 K (4 and 2 Bar). As shown in Figure 6, rate constants obtained at the lower pressure of each set (upward triangles) are significantly smaller than the corresponding result at higher pressure (downward triangles) and are claimed to be below the high-pressure limit.¹⁸ Such a large difference between measured rate constants when the pressure was changed only by a factor of 2 or 3 is very surprising for the rate constants that should be near the high-pressure limit. Indeed, expression (7) yields a very weak change of the rate constant in the fall-off region when approaching a high-

pressure limit. The differences between values calculated by using expression (7) for the three abovementioned pairs of experiments are $\approx 5\%$ (650 K) and $\approx 3\%$ (675 and 700 K) in contrast with a factor of 2.2 (650 K), 1.8 (675 K), and 2.5 (700 K), respectively as reported by authors¹⁸ and shown in Figure 6 with downward and upward triangles respectively. Vice versa, as expected, expression (7) would yield the values of $k_E(T)$ shown as upward triangles at much smaller pressures of 0.06 Bar (650 K), 0.08 Bar (675 K), and 0.1 Bar (700 K), respectively. This is consistent with authors' calculations indicative of 0.1 Bar as the appropriate pressure for smaller rate constants obtained at these three temperatures. The reason for these discrepancies is not clear but the discussed difference in the measured rate constants is actually below the two standard error uncertainty at 675 and 700 K and barely exceeds the combined uncertainty only at 650 K.

4 | SUMMARY

Kinetics of the OH addition reactions with isomers of 2butene and 2,3-dimethyl butene have been studied over the temperature range between 220 and 370 K and pressure range between 5 and 300 Torr. The rate constants for the reactions with the 2-butenes exhibit pressure dependences, which are more pronounced at higher temperatures and depend on the nature of the inert bath gas. In contrast, the rate constant of the OH addition to 2,3-dimethyl butene is pressure independent under these conditions. This suggests that the OH addition to alkenes as large as C4 is still in the fall-off regime, whereas OH addition to C6 alkenes is already at high pressure limit under such conditions.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article. **How to cite this article:** Orkin VL, Khamaganov VG, Kurylo MJ. Experimental kinetic study of the reactions between OH radicals and three 2-butenes over the temperature range 220–370 K and pressure range 0.67–40 kPa (5–300 Torr). *Int J Chem Kinet*. 2023;55:221–237. https://doi.org/10.1002/kin.21630

Supplementary Information.

Experimental Kinetic Study of the Reactions Between OH Radicals and Three

2-Butenes over the Temperature Range 220 K to 370 K and Pressure Range

0.67 kPa to 40 kPa (5 Torr to 300 Torr).

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IR absorption spectra of 2-Butenes and inter-isomer contamination of samples.

IR absorption cross spectra of *cis*-2-butene and *trans*-2-butene were measured by using our instrument previously described in detail.^{S1} The IR absorption spectra were measured by using an FTIR spectrophotometer Nicolet 6700 equipped with a (10.2 ± 0.05) cm glass absorption cell fitted with KBr windows. Spectra were measured with spectral resolutions of 0.125 cm⁻¹ by using a low-temperature MCT detector (between 650 cm⁻¹ and 3400 cm⁻¹) and 0.25 cm⁻¹ by using an ambient temperature DTGS detector (between 500 cm⁻¹ and 1350 cm⁻¹). Spectra were measured for pure 2-Butene pressures in the absorption cell ranging from 10 Torr (0.67 kPa) to 960 Torr (129 kPa). Spectral intervals with the measured absorbances less than 0.7 were stitched to obtain the combined spectrum of the compound over the entire range between 450 cm⁻¹ and 3400 cm⁻¹. Thusly obtained spectra of 2-butenes samples are presented in Figure S1 and S2.

GC-MS analysis is not capable in resolving and identification of small stereo-isomeric impurities in the samples of 2-butenes. Analysis of their IR spectra allows estimating cross-isomer contamination of samples of both *cis*-2-butene and *trans*-2-butene. Inserts in both Figure S1 and Figure S2 illustrate such analysis.

A very weak absorption band found in the IR spectrum of *trans*-2-butene sample between 630 cm⁻¹ and 710 cm⁻¹ exactly matches one of the main absorption bands of *cis*-2-butene. Insert in Figure S1 shows the spectrum of *cis*-2-butene (blue) and the spectrum of *trans*-2-butene increased by a factor of 100 (red) for comparison. From the comparison of integrated absorption over this range, we found $\approx 0.55\%$ of *cis*-isomer in the sample of *trans*-2-butene.



Figure S1. Absorption cross sections of (*E*)-2-Butene measured at 296 K with spectral resolution of 0.125 cm⁻¹ ($870 \text{ cm}^{-1} - 3300 \text{ cm}^{-1}$) and 0.25 cm⁻¹ ($500 \text{ cm}^{-1} - 870 \text{ cm}^{-1}$)



There is no similarly favorable spectral range to analyze *cis*-2-butene contamination with a small amount of *trans*-isomer. We analyzed a possible appearance of the small absorption feature of *trans*-2-butene between 1285 cm⁻¹ and 1325 cm⁻¹ on the smooth decreasing tail of *cis*-2-butene absorption band. Insert in Figure S2 shows the measured spectrum of cis-2-butene (blue). Two red lines present calculated spectrum when *trans*-2-butene is added in the amount of 1% and 0.3%, respectively. Two green lines present calculated spectrum when corrected for the possible presence of *trans*-2-butene in the amount of 0.3% and 1%, respectively. This simulation supports the suggestion that the possible presence of *trans*-2-butene is noticeably smaller than 1% and can be more or less realistically estimated as 0.3% as the corresponding green line

exhibits no visible presence of the trans-isomer's absorption band. Note, that even much more conservative estimate (<1%) cannot affect results of OH reaction rate constant measurements because of similar reactivity of both stereo isomers.



Figure S2. Absorption cross sections of (Z)-2-Butene measured at 296 K with spectral resolution of 0.125 cm⁻¹ ($820 \text{ cm}^{-1} - 3300 \text{ cm}^{-1}$) and 0.25 cm⁻¹ ($500 \text{ cm}^{-1} - 820 \text{ cm}^{-1}$)

Insert. Measured absorption cross sections of (Z)-2-Butene (blue) and results of addition (red) and subtracting (green) 0.3% and 1% of (E)-2-Butene's absorption cross sections.

IR absorption spectra of (Z)-2-Butene and (E)-2-Butene

Digitized IR spectra of trans-2-Butene and cis-2-Butene are presented in separate files after

correction for the presence of CO₂ in the sample *cis*-2-buten and the presence of CO₂ and 0.55%

of cis-2-buten in the sample of trans-2-butene.

Reference:

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