Shock tube measurements of high temperature rate constants for OH with cycloalkanes and methylcycloalkanes

R. Sivaramakrishnan, J.V. Michael *

Chemical Sciences and Engineering Division, D-193, Bldg. 200, Argonne National Laboratory, Argonne, IL 60439, USA

ABSTRACT

High temperature experiments were performed with the reflected shock tube technique using multi-pass absorption spectrometric detection of OH radicals at 308 nm. The present experiments span a wide T-range, 801–1347 K, and represent the first direct measurements of the title rate constants at $T > 500$ K for cyclopentane and cyclohexane and the only high temperature measurements for the corresponding methyl derivatives. The present work utilized 48 optical passes corresponding to a total path length ~4.2 m. As a result of this increased path length, the high [OH] detection sensitivity permitted unambiguous analyses for measuring the title rate constants. The experimental rate constants in units, cm^3 $molecule^{-1}$ s^{-1}, can be expressed in Arrhenius form as

$k_{OH+Cyclopentane} = (1.90 \pm 0.30) \times 10^{-10} \exp(-1705 \pm 156 \text{ K}/T)$ (813–1341 K),

$k_{OH+Cyclohexane} = (1.86 \pm 0.24) \times 10^{-10} \exp(-1513 \pm 123 \text{ K}/T)$ (801–1347 K),

$k_{OH+Methylcyclopentane} = (2.02 \pm 0.19) \times 10^{-10} \exp(-1799 \pm 96 \text{ K}/T)$ (859–1344 K),

$k_{OH+Methylcyclohexane} = (2.55 \pm 0.30) \times 10^{-10} \exp(-1824 \pm 114 \text{ K}/T)$ (836–1273 K).

These results and lower-T experimental data were used to obtain three parameter evaluations of the experimental rate constants for the title reactions over an even wider T-range. These experimental three parameter fits to the rate constants in units, cm^3 $molecule^{-1}$ s^{-1}, are

$k_{OH+Cyclopentane} = 1.390 \times 10^{-16} T^{1.779} \exp(97 \text{ K}/T)$ cm^3 $molecule^{-1}$ s^{-1} (209–1341 K),

$k_{OH+Cyclohexane} = 3.169 \times 10^{-16} T^{1.679} \exp(119 \text{ K}/T)$ cm^3 $molecule^{-1}$ s^{-1} (225–1347 K),

$k_{OH+Methylcyclopentane} = 6.903 \times 10^{-18} T^{2.148} \exp(536 \text{ K}/T)$ cm^3 $molecule^{-1}$ s^{-1} (296–1344 K),

$k_{OH+Methylcyclohexane} = 2.341 \times 10^{-18} T^{2.325} \exp(602 \text{ K}/T)$ cm^3 $molecule^{-1}$ s^{-1} (296–1273 K).

High level electronic structure methods were used to characterize the first three reactions in order to provide reliable extrapolations of the rate constants from 250–2000 K. The results of the theoretical predictions for OH + cyclohexane and OH + methylcyclopentane were sufficient to make a theoretical prediction for OH + methylcyclohexane. The present recommended rate expressions for OH with cyclohexane, and methylcyclohexane, give rate constants that are 15–25% higher (over the T-range 800–1300 K) than the rate constants utilized in recent modeling efforts aimed at addressing the oxidation of cyclohexane and methylcyclohexane. The current measurements reduce the uncertainties in rate constants for the primary cycloalkane consumption channel in a high temperature oxidation environment.

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1. Introduction

Cycloalkanes are an important class of hydrocarbons that are present in significant amounts in commercial transportation fuels such as gasoline, diesel, and jet fuels. Recent record prices for crude oil make fuels derived from the large deposits of tar sands and oil shale [1] an economically viable option. Their use

* Corresponding author. Fax: +1 630 252 4470.
  E-mail address: jmichael@anl.gov (J.V. Michael).

also reduces the dependence on imported oil into the US [2] thereby contributing to energy security. However, commercial fuels derived from these emerging sources of crude are expected to have increasing contents of cycloalkanes [3], and this will no doubt ultimately effect the combustion and emissions performance in transportation vehicles and fixed industrial combustors. These cycloalkanes also form aromatic hydrocarbons that are soot precursors through dehydrogenation [4]. Consequently, in recent years there has been significant activity within the combustion chemistry community to understand decomposition and oxidation routes resulting in the development of detailed predictive chemical kinetics models in order to design more efficient combustion systems.

Recent experimental and modeling studies [5,6] on the combustion of methylcyclohexane (a primary fuel surrogate) reveal that the reaction of OH with fuel is not only the dominant fuel decay channel under typical engine conditions, but also, simulations of lab scale experiments from shock tubes, reactors, and rapid compression machines (RCM) display sensitivity to this channel even under high-T conditions (>1200 K) where only thermal decomposition and subsequent small molecule reactions would be expected to display sensitivity. A brief survey of the NIST chemical kinetics [7] database reveals that there is a lack of high temperature studies (>500 K) for OH + cycloalkanes with the only exceptions being the Bott and Cohen [8] single point measurement of the OH + cyclopentane rate at 1200 K and the studies by Walker and co-workers [9,10] at 753 K. In the case of the methylcycloalkanes only room-T measurements are available. This paucity of data supplies the motivation for the present study. Consequently, we have performed direct measurements of high-T ($\sim$800–1300 K) rate constants for OH with cyclopentane (CP), cyclohexane (CH), methylcyclopentane (MCP), and methylcyclohexane (MCH) using tBH (*tert*-butyl hydroperoxide) as the OH source. The title reactions have also been theoretically investigated using electronic structure theory calculations. The energetics and the molecular parameters from these electronic structure calculations were subsequently used to compute theoretical rate constants with conventional transition state theory (CTST), including branching ratios for the various abstraction channels in the methylcycloalkanes.

2. Experiment

The present experiments were performed with the reflected shock tube technique using OH-radical electronic absorption. The methods and the apparatus currently being used have been previously described [11,12] and only a brief description of the experiment will be presented here. The shock tube was fabricated from 304 stainless steel in three sections. The first section, a 10.2 cm-o.d. cylindrical tube, was separated from the He driver chamber by a 4 mil unscored 1100-H18 aluminum diaphragm, and a second 0.25 m transition section then connected the first and third sections. The third section was of rounded corner (radius, 1.71 cm) square design and was fabricated from flat stock (3 mm) with a mirror finish. The tube was routinely pumped between experiments to less than 10^{-8} Torr by an Edwards Vacuum Products Model CR100P packaged pumping system. Incident shock wave velocities were measured with eight equally spaced pressure transducers (PCB Piezotronics, Inc., Model 113A21) mounted along the third section and recorded with a 4094C Nicolet digital oscilloscope. As given previously, corrections for boundary layer perturbations have been applied [13–15] for determining both temperature and density in the reflected shock wave regime.

For OH detection at 308 nm, a White cell, radially located at 6 cm from the endplate (as described previously [16–18]) was used to increase the absorption path length. It was constructed from two flat fused silica windows (3.81 cm), mounted on the

tube across from one another, with broadband antireflection (BB AR) coating for UV light. The distance between windows was 8.745 cm. The optical configuration consisted of an OH resonance lamp [16,17], multi-pass reflectors, an interference filter at 308 nm, and a photomultiplier tube (1P28) all mounted external to the shock tube. The photomultiplier signal was recorded with a LC334A LeCroy digital oscilloscope. At the entrance to the multipass cell, OH resonance radiation was collimated with a set of lenses and was focused onto the reflector on the opposite side of the shock tube through the two AR coated windows that were flush mounted to the inside of the shock tube. The reflectors and windows were obtained from the CVI Laser Corporation. These reflectors were attached to adjustable mounts, and the center points of windows and mirrors were all in a coaxial position. With this new configuration, 48 multiple passes were used, thereby amplifying the measured absorbances by about a factor of $\sim$4.5 over that used in the previous work [17,18]. This increase in sensitivity for OH-radical detection allows for the detection of lower [OH] and therefore decreases the importance of secondary reaction perturbations.

2.1. Gases

High purity He (99.995%), used as the driver gas, was from AGA Gases. Scientific grade Kr (99.999%), the diluent gas in reactant mixtures, was from Spectra Gases, Inc. The $\sim$10 ppm impurities (N_2—2 ppm, O_2—0.5 ppm, Ar—2 ppm, CO_2—0.5 ppm, H_2—0.5 ppm, CH_4—0.5 ppm, H_2O—0.5 ppm, Xe—5 ppm, and CF_4—0.5 ppm) are all either inert or in sufficiently low concentration so as to not perturb OH-radical profiles. The microwave driven OH lamp operated at 70 watts and $\sim$25 Torr pressure. Distilled water, evaporated at one atmosphere into ultra-high purity grade Ar (99.999%) from AGA Gases, was used in the resonance lamp. The hydrocarbon reactant molecules, cyclopentane, cyclohexane, methylcyclopentane, and methylcyclohexane, were obtained from Sigma Aldrich. The respective purities of all of these molecules were $\geqslant$99.5, $\geqslant$99.9, $\geqslant$99.5 and $\geqslant$99.5% but were further purified by bulb-to-bulb distillation, retaining only middle thirds for mixture preparations. The OH source molecule was *tert*-butyl hydroperoxide (tBH). tBH was obtained from Sigma Aldrich as a water solution (T-HYDRO tBH, $\sim$70% tBH by weight; i.e., $\sim$32 mol% tBH and 68 mol% H_2O) and used as the OH-radical source for the OH + hydrocarbon reaction studies as described previously [19,20]. The gas mixtures were accurately prepared from pressure measurements using a Baratron capacitance manometer and were stored in 22 l glass bulbs in an all glass vacuum line. The details of the mixture mole fractions used in the present experiments are available in Tables 1–4.

3. Results

Fig. 1 shows two typical [OH] profiles near the limiting high- and low-T regimes available using tBH as the OH source. tBH dissociation becomes too slow at $\sim$800–850 K. At reflected shock temperature $\sim$1300–1350 K, dissociation in the incident shock regime occurs complicating the analysis thereby limiting the upper temperature range. The profiles shown in Fig. 1 were obtained with cyclopentane as the reactant species. The lines shown in the figure are fits using our 50 reaction-30 species mechanism [20] with OH + cyclo-C_5H_{10} included as the main loss process for OH. A few reactions were also added to reflect possible perturbing reactions that might be specific to cyclopentane (e.g., cyclo-C_5H_{10} isomerization to 1-pentene [21], 1-pentene dissociation to $C_3H_5 + C_2H_5$ [21] and $C_3H_6 + C_2H_4$ [21], and reactions of C_3H_6 [22], C_3H_5 [23], and C_2H_5 [24] with OH). For the [tBH]$_0$ used in the present study, secondary reactions were found to be