Kinetics of oxidation of cyclohexanone in a jet-stirred reactor: Experimental and modeling

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Abstract

The kinetics of oxidation of cyclohexanone (CAS 108-94-1) was studied experimentally in a fused silica jet stirred reactor (JSR) for the first time. The experiments were performed in the temperature range 530–1220 K, at an operating pressure of 10 atm, for equivalence ratios ranging from 0.5 to 4, and with an initial fuel concentration of 1000 ppm ($\varphi = 0.5$, 1.0 and 2.0) and 1500 ppm ($\varphi = 4.0$). Concentration profiles of reactants, stable intermediates and products were measured at fixed residence time and variable temperature by gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR) after sonic probe sampling. Cyclic intermediates experimentally observed include, 2-cyclohexen-1-one, cyclopentene, cyclopentadiene and aromatics such as benzene and toluene, the latter in trace amounts only for rich mixtures. The experimental data were used to validate a detailed kinetic reaction mechanism. A reasonable agreement between the present experimental results and the computations was observed. Kinetic analyses (sensitivity and reaction paths) were used to interpret the results.
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1. Introduction

The combustion of fossil fuels for ground transportation significantly contributes to pollutants emissions and global warming through increasing atmospheric CO_2 concentrations [1–4]. Over the last decades the inclusion of non-fossil components in automotive fuels has increased [5] and mixtures of oil-derived fuels with a variety of oxygenates is used worldwide to mitigate carbon footprint [6]. Besides ethanol, which is a major gasoline component contributing to urban pollution increase via acetaldehyde emissions yielding tropospheric ozone formation [7–13], cyclic oxygenates have received attention. Cyclohexanone is a representative cyclic ketone that was identified as an interesting second generation fuel [14]. In studies carried out on heavy-duty diesel engines, Boot [14,15] Klein-Douwel [16] and co-workers showed that cyclohexanone blended synthetic Fischer–Tropsch fuel resulted in lower soot production. However, no previous studies on the kinetics of oxidation of that fuel could be

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found in the literature. To the best of authors' knowledge, the first studies on cyclohexanone date back to 1930s and were on photochemical decomposition of cyclic ketones by Norrish et al. [17,18] and a pyrolytic study performed by de Mayo and Verdun [19] published in 1970. Mayo and Verdun studied the thermal fragmentation of this compound in a flow system at 1050 °C, they reported methyl vinyl ketone as the major decomposition product among other stable species observed, including cyclopentane and 1,3-cyclopentadiene.

As part of a continuing laboratory effort to improve the knowledge of the kinetics of biofuels combustion and provide necessary inputs for chemical kinetic modeling, we (i) performed experiments on the oxidation of cyclohexanone in a jet-stirred reactor (JSR) at elevated pressure, over a wide range of equivalence ratios and temperatures, (ii) built a cyclohexanone oxidation kinetic sub-scheme (iii) tested the validity of the proposed kinetic reaction mechanism against our data. The present experimental and modeling results are reported in the next sections.

2. Experimental

A fused-silica JSR similar to that used previously [20] and operating up to 10 atm was used. It was located inside a regulated electrical resistance oven of ≈ 3 kW itself surrounded by insulating ceramic wool and a stainless steel pressure-resistant jacket. Cyclohexanone (99.8% pure, Aldrich) was used in the experiments. The liquid fuel was pumped, using a micro piston HPLC pump (Shimadzu LC-120 ADvp) equipped with an on-line degasser (Shimadzu DGU-20 A3). The fuel was sent to an in-house stainless steel atomizer-vaporizer assembly maintained at 200 °C. A flow of nitrogen (50 L/h) was used for the fuel atomization. The oxygen (99.995% pure, Air Liquide) flow was diluted by a flow of nitrogen (<50 ppm of O_2; <1000 ppm of Ar; <5 ppm of H_2, Air Liquide). This oxygen–nitrogen flow was mixed with the fuel-nitrogen flow just before the entrance of the injectors, after preheating. All the gases were regulated by thermal mass-flow controllers (Brooks 5850E). Residence time distribution studies have shown that under the conditions of the present study the reactor is operating under macro-mixing conditions[20]. As in previous work [20,21], temperature measurements were performed using a 0.1 mm diameter Pt/Pt-Rh 10% thermocouple (the wires were isolated inside a thin-wall fused-silica tube to prevent catalytic reactions on their surface). These measurements showed good thermal homogeneity along the vertical axis of the reactor. Temperature gradients of less than 2 K/cm were measured. Given that the experiments were performed under high

dilution, the temperature rise due to fuel oxidation was generally <ca. 30 K. Low pressure samples of the reacting mixtures were taken by sonic probe sampling and collected in 1 liter Pyrex bulbs at ca. 50 mbar for immediate GC analyses, as done before [21–23].

Hydrocarbons and oxygenates were analyzed on capillary columns of 0.32 mm i.d. (DB-624, 50 m and Al_2O_3/KCl, 50 m) with a flame ionization detector and helium as carrier gas. Hydrogen and oxygen were measured using a 0.53 mm i.d. capillary column (Carboplot, 25 m) fitted to a thermal conductivity detector. Nitrogen was used as carrier gas. Additionally, on-line FTIR analyses of the reacting gases were done by connecting the sampling probe, via a Teflon heated line kept at 210 °C, to a temperature-controlled gas cell maintained at 140 °C. The sample pressure in that 10 m path-length cell was 0.2 bar and a 0.5 cm^{-1} resolution was used for the data acquisition. This analytical equipment allowed the measurements of the reactants (oxygen and cyclohexanone), and products, i.e., hydrogen, H_2O, CO, CO_2, methane, formaldehyde, ethane, ethylene, acetylene, acetaldehyde, propene, acrolein, 1-butene, 1,3-butadiene, methyl vinyl ketone, 1,3-cyclopentadiene, cyclopentene, 2-cyclohexen-1-one, and also 1,5-hexadiene, benzene, styrene (less than 10 ppm). Very good agreement between the GC and FTIR analyses was observed for the compounds measured by both techniques. Carbon balance was checked for every sample and found to be good (typically $100 \pm 10\%$). Hydrogen balance was found to be within $\pm 10\%$ (e.g. for $\varphi = 4$ mixture with 0.15% fuel, this corresponds to ± 1500 ppm on H-balance). Oxygen balance is within 5% for most of the experimental points except for the richest mixture at $T > 1130$ K where oxygen balance exceeds 10% leaving an uncertainty of about 1250 ppm on the O atom, which is possibly related to the O_2 measurement. Uncertainty on temperature measurements was estimated to be less than 10 K, on residence time was less than 5%, on reactor pressure ± 0.1 atm and uncertainty related to the analytical technique is less than a ppm. Inlet uncertainties are less than 5% for the reactants; for measured species an uncertainty of <10% was determined for those with concentrations higher than 10 ppm. These factors contribute to an uncertainty of the mole fractions of the species, the exact amount of which is difficult to evaluate. A spreadsheet of the present experimental dataset is provided as Supplementary material.

3. Kinetic modeling

The chemical kinetic modeling was performed using the PSR computer code [24]. We introduced a sub-scheme for cyclohexanone pyrolysis and oxidation in our detailed kinetic reaction