



Experimental and Theoretical Study of Cyclopentanone as a Catalyst for Low Temperature Alkene Oxidation

Preprint

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Experimental and Theoretical Study of Cyclopentanone as a Catalyst for Low Temperature Alkene Oxidation

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Abstract: Cyclopentanone was evaluated for spark-ignition fuel properties to determine potential as a bio-blendstock. Although key properties such as octane numbers and energy density are promising, when blended with commercial gasoline the oxidation stability was significantly reduced. Oxidation stability determination exposes fuel to mild oxidative conditions of 700 kPa oxygen followed by temperature increase to 100 °C, resulting in a final pressure of ~ 900 kPa. Oxygen consumption is determined by monitoring for decrease in pressure over time – the results evaluate potential for autoxidation during storage. An increase in oxidation rate from cyclopentanone was not anticipated given the relatively low reactivity of this compound. Detailed hydrocarbon analysis of blends before and after oxidation revealed cyclopentanone was not consumed, but alkenes were oxidized to a significantly higher degree with this compound present. Experiments with surrogate blends of isooctane, cyclopentanone, and linear isomers of hexene demonstrated that cyclopentanone catalyzes alkene oxidation to form epoxides under mild oxidative conditions. This unexpected behavior observed may have implications in low temperature combustion of alkenes when ketone fuels are present, as well as epoxidation chemistry. This study proposes a detailed mechanism for a catalytic cycle evaluated with quantum chemical calculations performed with density functional theory.

Keywords: *Biofuels, Oxidation, DFT, Cyclopentanone*

1. Introduction

Cyclopentanone was evaluated as a gasoline range bio-blendstock as part of the U.S. Department of Energy's Co-optimization of Fuels and Engines (Co-optima) initiative [1]. Key properties such as volatility, octane numbers, and energy density appear promising for this molecule [1]. It was noted; however, that cyclopentanone (CP) decreased the oxidation stability of the gasoline blendstock used to prepare blends in this study. The mechanism by which CP reduced stability was not determined, but it was speculated that CP itself may undergo self-condensation under these conditions leading to oxygen consumption and formation of polymeric materials [2].

Oxidation stability of gasoline is evaluated by heating a sample in the presence of oxygen pressure and monitoring for oxygen consumption via pressure decrease. When oxygen consumption rate becomes rapid, this indicates the breaking point (a.k.a. induction period), typically expressed in minutes or hours. This assessment of oxidative resistance (also referred to as oxidative reserve) provides a relative measure of resistance to gum formation and fuel quality degradation during storage and handling. Fuels with more reactive components, such as olefins, perform more poorly

on this test [3-5]. The ASTM specification for spark ignition fuels, D4814, includes the requirement that fuels be tested by standard method D525 and have an induction period of 240 minutes or higher [6]. This limit is based on historical experience with gasoline range fuels but is not correlated to composition or storage conditions. Fuels having higher than the minimum induction period are said to have acceptable short-term stability.

CP was found to decrease oxidation stability when blended into gasoline. This oxygenate therefore may have potential to promote fuel quality degradation if used as a gasoline bio-blendstock. The mechanism by which CP promotes poor oxidation stability results has not been evaluated previously. This study examines the oxidative behavior of CP under relatively mild conditions, characterizes species formed during low temperature oxidation, and provides insight into the likely mechanism taking place.

2. Methods / Experimental

Liquid samples were oxidized following ASTM D525 Standard Test Method for Oxidation Stability of Gasoline. Samples were placed in a pressure vessel which was then filled to 700 kPa oxygen, followed by heating to 100 °C. Pressure was continuously recorded for 24 hours. An oxidation break point (a.k.a. induction period) is defined as the point in time at which oxygen consumption rate first exceeds 14 kPa in 15 min. The amount of residue formed during oxidation was determined by ASTM D873, which exposes the sample to the same conditions as D525 followed by filtration and weighing of insoluble material. Detailed hydrocarbon analysis (DHA) was performed on the remaining liquid after D525 oxidation experiments. This analysis is based on gas chromatography (GC) with flame ionization detection (FID). The GC column and instrument parameters followed ASTM D6729 Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Meter Capillary High Resolution Gas Chromatography. In addition to this standard method, samples were also analyzed by GC with mass spectrometry (GC-MS) to identify oxygenated species formed and verify compounds detected by GC-FID. Oxygenated compounds identified by GC-MS were quantified by GC-FID using response factors calculated by the effective carbon method [7]. The concentrations of oxygenates is therefore considered somewhat approximate.

A reformulated blendstock for oxygenate blending (RBOB) was used to prepare a 20 vol% blend with cyclopentanone (CP). Model compound blends were also prepared in isooctane: 20 vol% CP, 20 vol% 1-hexene, and 20 vol% trans-2-hexene. Combined blends of a single hexene isomer and CP were prepared at 20 vol% of each component with the balance being isooctane. Isooctane, hexene isomers, and CP were purchased from Sigma-Aldrich at purities $\geq 99\%$.

The mechanism of oxidation was evaluated using quantum chemical calculations performed with density functional theory (DFT). All these calculations were performed using Gaussian 16 package. All geometries including reactants, intermediates, transition states and products were optimized with the LC-wPBE functionals and the 6-31G(2df,p) basis sets. Each transition structure confirmed only one imaginary frequency and intrinsic reaction coordinate (IRC) calculations were also performed to confirm relevant reactant and product complexes.

3. Results and Discussion

The base fuel used in blending experiments, RBOB, did not exhibit an induction period within the 24 hours of exposure to oxygen, pressure, and heat. When this same RBOB was blended with 20 vol% CP, the oxidation stability was reduced such that an induction period was established at 391 minutes. This result exceeds the minimum oxidation stability required by ASTM D4814, but also indicates a significant decrease in stability with this added oxygenate. Table 1 provides the induction period for these samples as well as the maximum and minimum pressures recorded.

Initially, it was assumed that CP itself was reacting, resulting in a lower stability for the blend relative to the base RBOB. An experiment was performed with 20 vol% CP in isooctane to isolate the oxidation behavior of this compound. This test showed no induction period within 24 hours. The tendency to form insoluble material was also evaluated by ASTM D873, which resulted in a low amount of insoluble material not indicative of gum formation. No evidence of reaction was observed with CP in a blend with isooctane alone.

Table 1: ASTM D525 oxidation stability results.

Fuel Sample	Max Pressure (kPa)	Min Pressure (kPa)	% Pressure decrease from max	Induction Period (min)
Base RBOB	919	714	22.3	> 1,440
20% Cyclopentanone/RBOB Blend	907	237	73.9	391
20% CP/Isooctane (IO) Blend	893	840	5.9	> 1,440
20% 1-Hexene/IO Blend	868	826	4.8	> 1,440
20% 1-Hexene/20% CP/IO Blend	865	234	73.0	582
20% Trans-2-Hexene/20% CP/IO Blend	856	269	68.6	311

DHA was conducted on a 20% CP/RBOB blend before and after oxidation to provide insight into compositional changes occurring. The results of this experiment (Fig. 1) showed the concentration of CP did not significantly change during oxidative exposure. There was a small decrease in lower molecular weight/higher volatility paraffins and isoparaffins related to evaporation during venting of the pressure vessel, as well as an increase in aromatics and naphthenes relative to loss of these paraffins and isoparaffins. There was a small apparent increase in CP, also related to evaporation of the lightest material. The most significant change in composition was olefin concentration. This decreased by 18% for the RBOB, while the 20% CP/RBOB blend showed an olefin decrease of 52%.

The most abundant oxygenates detected after oxidation experiments are provided in Table 2 along with their concentrations and structures. Notably, the most abundant oxygenate, 2,2,3-trimethyloxirane, is consistent with epoxidation of the most abundant olefin identified in the RBOB DHA, 2-methyl-2-butene.

Oxidation of CP has been studied in a jet stirred reactor in the temperature range of 730-1280 K and pressures from 1-10 atm [8]. Although these conditions are vastly different from the experiments for oxidation stability, these previously reported results may provide insight into expected oxidation products of CP. Initial species include cyclopentenones and ring opened

compounds such as linear aldehydes and ketones. These structures were not detected in these experiments. Oxygenated species detected were consistent with oxidation of olefins.

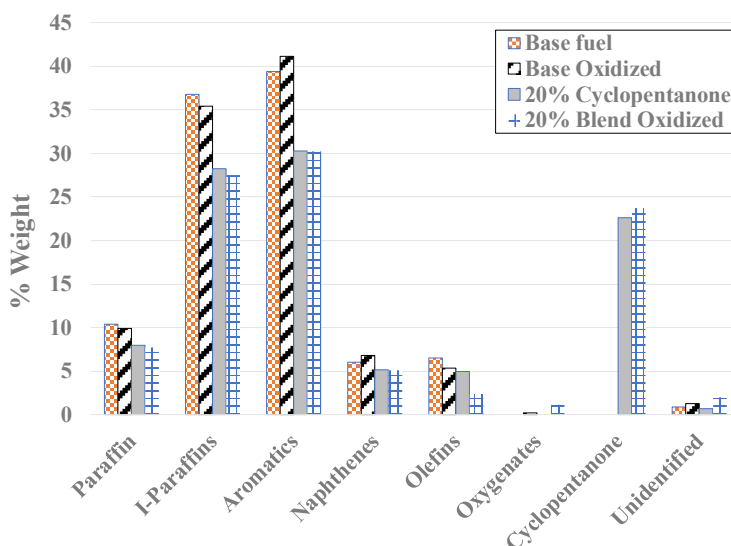


Figure 1: Detailed hydrocarbon analysis results for the gasoline base fuel (RBOB) and 20 vol% CP/RBOB blend before and after oxidation experiments

Table 2: Weight % of most abundant oxygenates detected in RBOB after oxidation with and without CP.

Oxygenates, Wt% approximate	Structure	RBOB	20% CP in RBOB
2,2,3-Trimethyloxirane		ND	0.33
2,2-Dimethyl-3-hydroxypropionaldehyde		0.02	0.13
Acetophenone		0.04	0.08
2-Phenyl-2-propanol		ND	0.08
3-Ethyl-2,2-dimethyl-oxirane		ND	0.06

ND = Not detected

Reactions between CP and olefins were studied with model compounds blended into isooctane as a low reactivity gasoline surrogate. Results of these experiments are provided in Table 1. A sample containing 1-hexene and isooctane in the absence of CP showed no reactivity in 24 hours while CP/1-hexene combined showed a considerable pressure drop and reached an induction period at 582 minutes. Similarly, trans-2-hexene in the presence of CP had an induction period of 311 minutes. DHA results for these samples are provided in Figure 2. As with RBOB blends, the largest change in composition was concentration of the olefin, while CP was not consumed in the reaction. The most abundant product detected from CP/1-hexene oxidation was 1,2-epoxyhexane, the epoxide of 1-hexene (Table 3). This compound was detected to a small degree without CP present but was in much higher concentration for the CP/1-hexene combined blend. Trans-2-hexene primarily produced trans-2-methyl-3-propyloxirane. A small amount of cis-2-methyl-3-propyloxirane was also detected. DHA of this sample before oxidation detected a small amount of cis-2-hexene, 0.04 wt%. After oxidation 0.37 wt% cis epoxide was measured indicating this was likely formed via isomerization of the trans olefin during epoxidation. The reaction is therefore not likely a stereospecific epoxidation reaction.

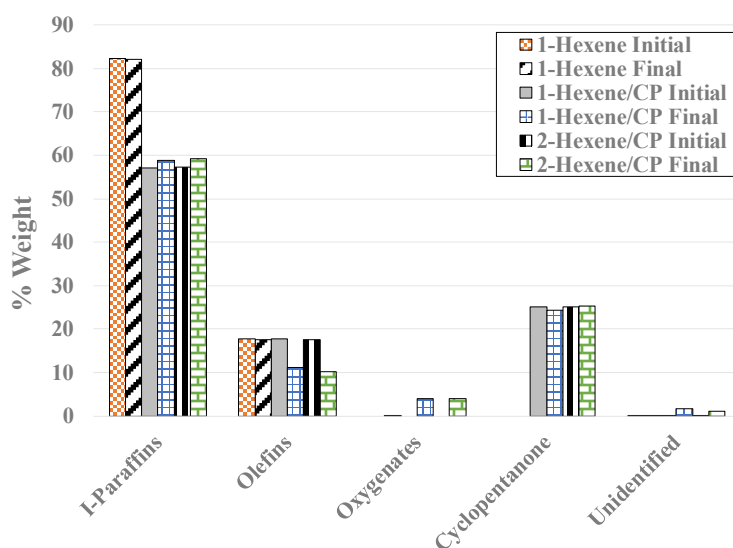


Figure 2: Detailed hydrocarbon analysis results for model compound blends prepared in isooctane

Ketone catalyzed epoxidation reactions are well documented, but typically require strong oxidants for efficient reactivity [9]. A small conversion percentage has been reported with cyclopentanone in the presence of hydrogen peroxide as an oxidant in a basic solution of acetonitrile [10]. In this case, only 5% conversion of methylstyrene was observed in 10 hours. This low efficiency of olefin conversion to an epoxide can similarly be seen in these oxidation experiments – approximately 40% of the olefin was consumed in 24 hours, with ~12% of this starting material becoming an epoxide. The remaining balance is accounted for by various other oxygenates and unidentified compounds.

Table 3: Weight % of most abundant oxygenates detected in isooctane blends after oxidation with and without CP.

Oxygenates, Wt% approximate	Structure	20% 1-Hexene	20% 1-Hexene/20% CP	20% Trans-2-hexene/20% CP
1,2-Epoxyhexane		0.02	2.17	ND
Pentanoic acid		ND	0.48	ND
Trans-2-methyl-3-propyl-oxirane		ND	ND	2.40
Cis-2-methyl-3-propyl-oxirane		ND	ND	0.37
3-Hexen-2-one		ND	ND	0.25
4-Hexen-3-one		ND	ND	0.18
Tert-butyl hydroperoxide		0.08	0.22	0.21

We performed DFT calculations to understand how olefins were oxidized in the presence of CP. Figure 3 shows our preliminary kinetic mechanisms with potential free energy diagrams. Propene was used instead of 1-hexene in this calculation to save computational cost. Dehydrated radical species of CP (**1**) was used as our starting point in this mechanism for a catalytic cycle and was treated as a catalyst. After the first O₂ addition (**2**), we compared propene addition (18.2 kcal/mol activation energy barrier) and HO₂ elimination reactions in the α -position (22.9 kcal/mol) [11]. Olefin addition (propene in this case) reactions are preferred by 4.7 kcal/mol lower activation energy. The first epoxidation step of the cycle occurs via an 18.0 kcal/mol activation energy barrier producing a thermodynamically stable intermediate (**5**). The second epoxidation reaction showed a 46.9 kcal/mol barrier to restart catalytic cycle. The entire catalytic cycle showed a significant downhill energy barrier by -48.9 kcal/mol which provides insight into how ketones affect low temperature oxidation of olefinic fuels. In addition to this preliminary mechanistic evaluation we are examining other possible pathways including the β -position of CP and other reactive radical species (e.g. CH₃, OCH₃).

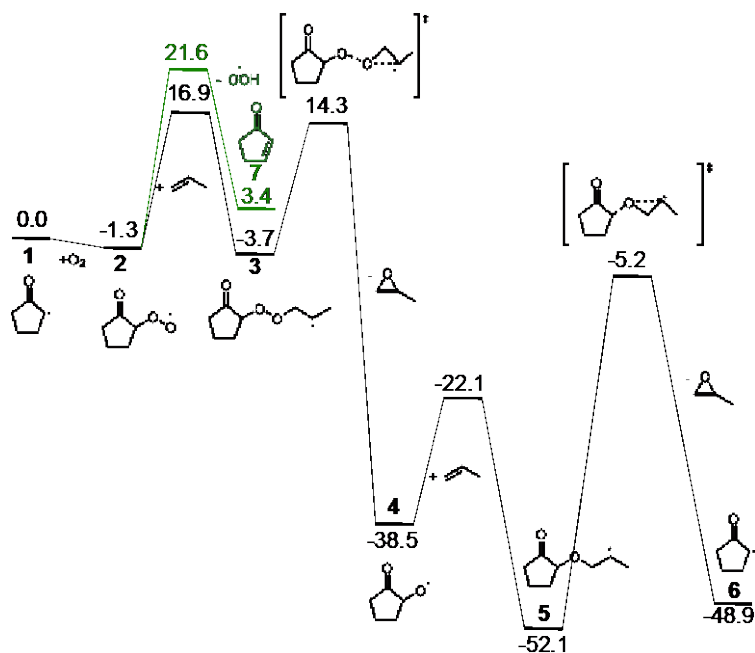


Figure 3: Potential mechanistic pathways with potential energy diagrams for CP catalyzed epoxidation of olefins (propene).

4. Conclusions

CP was found to reduce gasoline oxidation stability with standard screening methods. Detailed analysis of liquid samples after oxidation experiments revealed the production of epoxides from olefins in gasoline, while CP itself was not consumed. Experiments with model compounds has revealed that CP acts as a catalyst for olefin epoxidation under relatively mild oxidative conditions. These results show that CP may require additional consideration for handling and storage if used as a bio-blendstock for fuels. The ability for CP to promote olefin oxidation in oxygen rich conditions at low temperatures may also have implications in low temperature combustion and epoxidation reactions.

5. Acknowledgements

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