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UTTL: Ignition delay times of cyclopentene oxygen argon mixtures

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ABS: The oxidation of cyclopentene was studied experimentally to expand the
database on pyrolysis and the reaction products of five carbon unsaturated
ring compounds. Pyrolysis was carried out in a single-pulse shock tube.
Data were gathered on the shock speed, wall pressure, and reflected shock
temperatures. Four different mixtures of C₅H₈, O₂ and Ar, ranging from

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0.25-1 percent cyclopentene and 1.75-7 percent O₂, were examined in 76
different trials. The data showed a shock temperature range of 1323-1816 K
and a pressure range of 1.67-7.36 atmospheres. A student-t test analysis
of the results led to definition of an ignition delay equation accurate to
the 2-sigma level.

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IGNITION DELAY TIMES OF CYCLOPENTENE OXYGEN ARGON MIXTURES.

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The ignition delay times of cyclopentene with oxygen diluted in argon was investigated over a concentration range of 0.25 to 1% cyclopentene and 1.75 to 7% oxygen. The temperature range was 1323 - 1816K and the reflected shock pressures were 1.67 to 7.36 atmospheres.

Statistical evaluation of the experiments provide an over all equation with a 2σ confidence level as follows:

$$\tau = 5.86 \times 10^{-16} \exp(52770/RT) [C_5H_8]^{-0.59} [O_2]^{-1.61} [Ar]^{0.38} \text{ sec.}$$

Detailed experimental information is provided.

1. INTRODUCTION

It was undertaken to study the oxidation of cyclopentene as a representing member of five carbon unsaturated ring compounds. The five membered ring compounds should be closely related to the kinetics of aromatic compounds.

Over two decades of investigation in the problems of soot formation and the role of aromatic compounds in this process, as well as the kinetics of oxidation of aromatic compounds have not yet been able to provide decisive answers to the above questions. A few mechanisms have been proposed but no crucial evidence has yet been supplied to favor any of them. One of the first oxidation proposals for benzene was given by Assaba¹. Following this mechanism, phenyl radicals are formed from benzene which react to give biphenyl molecules, and these were supposed to be the precursors of soot. The oxidation steps that Assaba proposed were undecisive and he assumed the formation of a phenyl peroxy radical in the process of the ring opening.

Kern² who investigated the benzene pyrolysis with a mass spectrometer hooked to the shock tube, has shown that no phenyl and no biphenyl radicals and molecules are formed in the process. While the phenyl miss-appearance was blamed on the low sensitivity of Kern's system, the unavailability of biphenyl species seems real.

Glassman who investigated the oxidation of benzene in a flow reactor³, proposed a mechanism by which the benzene is transformed to five membered ring intermediates, such as cyclopentadiene, which continue to decompose further. Thus it is clear that five membered ring compounds may have an important role in the oxidation kinetics of aromatic compounds. Since a direct investigation on this subject is complex, an investigation of the individual kinetics of five member ring compounds may clear the mechanism of the oxidation of aromatic compounds.

2. EXPERIMENTAL

A single pulse shock tube was used to perform the experiments. The shock tube was made of stainless steel pipe, flattened to a 3 by 3 inch square tube with rounded corners. The tube was honed and polished on all inside surfaces. The dump tank was located at the end of the driver section and separated from the driver section by an aluminum diaphragm. A second aluminum diaphragm was located between the driver and the driven section. The two diaphragms were burst by an auxiliary short shock tube. This short shock tube had a third diaphragm that was burst by a hand plunger.

The shock speed was measured over two separate intervals using three pressure transducers whose signals were fed to a dual channel Nicolette transient recorder. The shock speed was measured with an accuracy of $\pm 0.1 \mu\text{sec}$. A Kistler pressure transducer was located in the side wall, 3 mm away from the end plate. This pressure transducer was connected to a second Nicolette transient wave recorder, and was used to record and measure the ignition delay time from the pressure history of the gas (See fig. 1). The ignition delay time was measured to $\pm 1 \mu\text{sec}$.

The mixtures were prepared in stainless steel tanks at 50 PSI total pressure using a separate manifold. The gases and vapors were measured manometrically and let to expand into preevacuated stainless steel tanks. Pure 3H Argon was used to pressurize the tank to 50 PSI. The mixtures were allowed to mix for 24 hours before use. Different mixtures of pure grade Airco Helium and 3H Argon were used as driver gases. The cyclopentene was spectroscopical grade reagent.

The reflected shock temperatures were calculated using standard conservation equations and the ideal gas equation of state assuming frozen chemistry. All the thermodynamic data used were taken from new compilations⁴

3. RESULTS AND DISCUSSION

The experiments were performed with four different mixtures A-D. In total 76 shocks were run. The exact groups of experiments are given in Table I. The mixture were prepared so that delineation of power dependencies could be done from an empirical ignition delay equation:

$$\tau = 10^{-x} \exp(+E/RT) [\text{Fuel}]^a [\text{O}_2]^b [\text{Ar}]^c \text{ sec.}$$

In each of the performed shocks, the mixture composition and initial properties are known. The post shock experimental properties were the reflected temperature T_2 , the density ratio ρ_2/ρ_1 and the ignition delay time τ . The experiments were spread over a wide temperature range to permit maximum sensitivity to the determination of the so called "activation energy". An eyeball straight line fit was drawn through the experimental points to help visualizing the following explanation.

TABLE I. Experimental Conditions of Cyclopentene Mixtures.

Series	Compositions			P ₁ torr	Number of experiments	Parameters determined
	%C ₅ H ₈	%O ₂	%Ar			
A	0.258	7.	92.74	50	22	a, b
B	0.25	1.75	98.0	50	13	b
C	0.333	2.33	97.33	150	25	c
D	1.0	7.0	92.00	50	16	a, c

Figure 2 presents series A and B in a $\log \tau$ vs. $1/T_g$ plot for cyclopentene. Mixtures A and B have a fourfold difference in the oxygen concentration. The distance between the lines is 0.98 logarithmic units. Therefore

$$\log \tau_A = a \log(0.25\% [C_5H_8]) + b \log(4 \times 1.75\% [O_2]) + c \log [Ar]$$

$$\log \tau_B = a \log(0.25\% [C_5H_8]) + b \log(1.75\% [O_2]) + c \log [Ar]$$

subtracting $\log \tau_B$ from $\log \tau_A$ and disregarding the differences in Ar concentrations we get

$$-\Delta \log \tau_{(A-B)} = b \log 4$$

$$b = \Delta \log_{(A-B)} / \log 4 = -0.98/0.6 = -1.63$$

Figure 3 consequently presents $\log \tau$ vs. $1/T_g$ for series A and D to get the cyclopentene power dependence following the former calculation

$$a = \frac{\Delta \log \tau_{(D-A)}}{\log 4} = \frac{0.317}{0.6} = 0.53$$

Figure 4 presents $\log \tau$ vs. $1/T_g$ for series C and D. In mixture C the concentration of the reactants is a third of that in mixture 4. But the pressure used was three times higher. Therefore the real concentrations of cyclopentene and oxygen are the same in both mixtures but the concentration of argon is three times higher in mixture C than in mixture D. The distance between the two lines in mixtures C and D is 0.216 $\log \tau$ units and therefore

$$c = \frac{\Delta \log \tau_{(C-D)}}{\log 3} = 0.45$$

The former discussion was used to explain why the mixtures were chosen as they were, and how the experiments were performed. It was found however that a statistical approach to the determination of a, b, and c was more appropriate and more accurate since it could take into consideration such factors as ρ_s/ρ_1 and differences in concentration of argon between the gas mixtures. These parameters

were neglected in the graphical presentation on figures 2-4. The statistical results given below point out that the neglected parameters change the results obtained in the graphical form.

Figure 5 shows the overall plot of $\log \beta$ vs. $1/T_s$ for a maximum acceptable spread of 2σ . The correlation was found with a statistical "student-t" program using 67 experiments.

$$\tau = 10^{-16.88 \pm .89} \exp(52770 \pm 1540/RT) [C_5H_8]^{0.69 \pm 0.07} [O_2]^{-1.61 \pm 0.07} [Ar]^{0.88 \pm 0.07} \text{ sec.}$$

The former reduced over all ignition delay equation is in good agreement with the graphical analysis shown above.

Table II contains a list of 5 representative shocks from each group performed in this study and their pre and post shock parameters.

The former value for cyclopentene should be compared with values found for benzene and toluene in a similar study⁵.

Table II Reflected Parameters and Results of Representative Shocks

Series	Composition %		Shock No	P_1 torr	ρ_2/ρ_1	T_s K	τ sec	P_2 atm
	C_5H_8	O_2						
A	0.258	7.0	8	50	5.85	1343	1007	1.72
			12	50	6.00	1398	530	1.84
			13	50	6.50	1595	42	2.27
			15	50	6.19	1467	156	1.99
			21	50	6.06	1419	342	1.89
B	0.25	1.75	102	50	6.88	1585	454	2.11
			105	50	6.27	1678	170	2.30
			108	50	6.53	1816	40	2.60
			111	50	5.99	1543	822	2.03
			113	50	5.85	1482	1632	1.90
C	0.333	2.33	201	150	6.08	1533	236	6.13
			202	150	5.78	1409	1054	5.36
			206	150	6.19	1581	153	6.44
			209	150	6.49	1724	44	7.36
			214	150	5.89	1450	767	5.61
D	1.00	7.00	302	50	6.77	1431	580	2.12
			304	50	6.70	1410	876	2.07
			306	50	7.20	1574	96	2.49
			310	50	7.68	1748	20	2.94
			313	50	7.00	1505	223	2.31

For benzene using a 2σ maximum acceptable spread from 80 experiments the over all ignition delay time found was

$$\tau = 9.0 \times 10^{-16} \exp(41450/RT) [C_6H_6]^{0.44} [O_2]^{-1.77} [Ar]^{0.44} \text{ sec.}$$

For toluene using 54 experiments we get the over all value of

$$\tau = 5.28 \times 10^{-16} \exp(55100/RT) [C_7H_8]^{0.55} [O_2]^{-1.38} [Ar]^{0.35} \text{ sec.}$$

while for cyclopentene the value is

$$\tau = 5.85 \times 10^{-16} \exp(52800/RT) [C_5H_8]^{0.59} [O_2]^{-1.61} [Ar]^{0.33} \text{ sec.}$$

The comparison with benzene shows a similar oxygen power dependence, a lower power dependence of argon i.e. a small third body inhibiting effect.

The inhibiting effect of argon was not encountered in simple hydrocarbons i.e. methane⁶, ethane⁷, propane⁸, propene⁹, and propyne¹⁰. It was however encountered in long chain hydrocarbons like heptane¹¹, and pseudo ring compounds like ethylene-oxide¹².

It was shown in earlier studies¹² that the inhibiting effect of the diluent occurs, because it acts as a heat sink to the heat evolving from the reaction. This heat can be identified with the process of shattering the ring. To open the ring a large amount of energy is needed. But part of this energy is absorbed by the diluent thus causing an inhibition to the reaction.

Benzene is harder to shatter than toluene and toluene, than cyclopentene, thus it is clear that the inhibiting effect will be lowered when going from one to the other.

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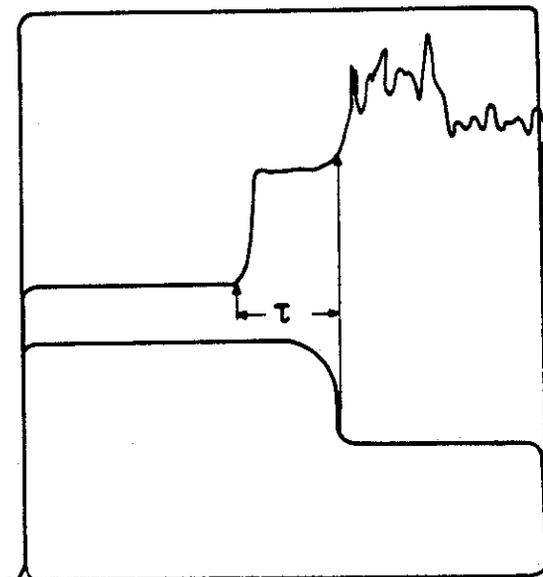


Figure 1. Pressure traces from which ignition delay times were determined.

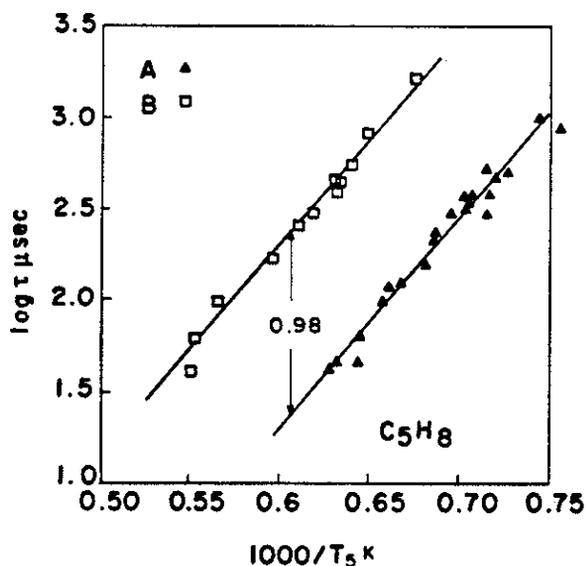


Figure 2. A plot of $\log \tau$ vs. $1/T_s$ for mixtures A and B, representing the oxygen power dependence.

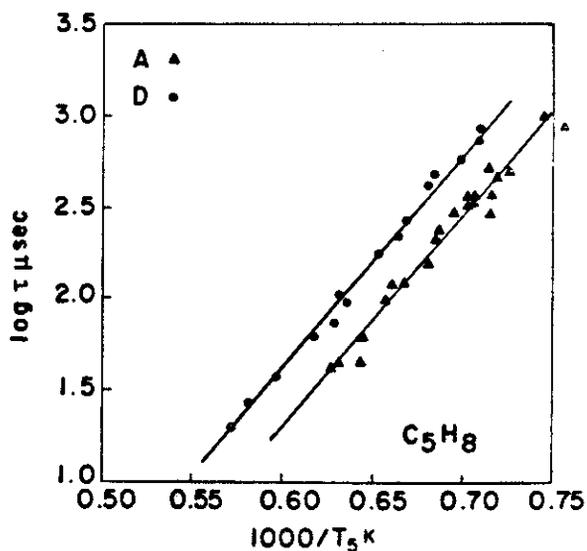


Figure 3. A plot of $\log \tau$ vs. $1/T_s$ for mixtures A and D, representing the cyclopentene power dependence.

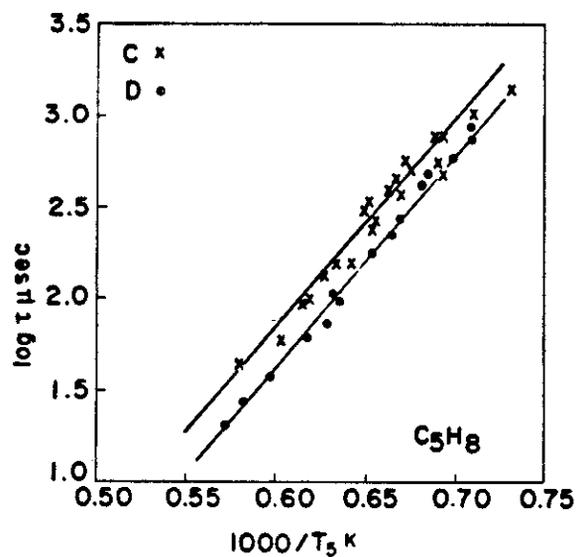


Figure 4. A plot of $\log \tau$ vs. $1/T_s$ for mixtures C and D, representing the argon dependence.

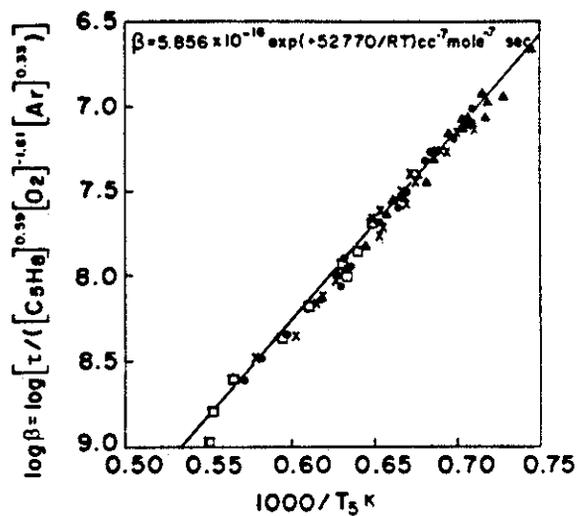


Figure 5. The plot of all experimental points as $\log \beta$ vs. $1/T_s$ for a maximum acceptable spread of 2σ .