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Catalytic Partial Oxidation of Cyclohexane in a Single-Gauze Reactor

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Cyclohexane oxidation in a single-gauze reactor can produce ∼85% selectivity to olefins and oxygenates at 25% cyclohexane conversion and 100% oxygen conversion, with cyclohexene and 5-hexenal as the dominant products. Experiments are performed with a 90% platinum–10% rhodium single gauze (∼90-μm wire diameter) at cyclohexane/oxygen (C_6H_{12}/O_2) molar ratios of 0.4 to 5.0, flow rates of 1 to 3 standard liters per minute, preheat temperatures of 100 to 300°C, N_2 dilution from 5% to the air composition, and pressures of 1.2 to 2 atm. The cyclohexane/oxygen ratio is the most important variable for operation of the single-gauze reactor because temperatures, reactant conversions, and product selectivities all change significantly as C_6H_{12}/O_2 is varied. Low dilution favors olefin production while high dilution suppresses the homogeneous reactions necessary for oxygenate formation. Oxygenates are also favored by high flow rates and low inlet temperatures. Higher reactor pressures (up to 2 atm) increase the yield of cyclohexene and 5-hexenal and allow complete oxygen conversion. Cyclohexanone can be produced with 5% selectivity at $C_6H_{12}/O_2 \approx 4$. Reaction pathways for cyclohexane partial oxidation are hypothesized, and the products are consistent with the proposed surface-assisted gas-phase sequences.

Key Words: **cyclohexane; partial oxidation; single-gauze reactor; oxygenates; short contact time.**

1. INTRODUCTION

Oxygen-containing hydrocarbons, or oxygenates, are typically produced at low temperature in the liquid phase through multistage processes involving expensive separations. The current methods for production of oxygenates require expensive catalysts, large residence times, and careful temperature control. Practical selectivities of desired oxygenated compounds can be obtained only at low conversions. A direct method that selectively produces oxygenates would be industrially significant for the manufacture of specialty chemicals.

In recent years, short-contact-time reactors employing Pt–10% Rh single-gauze catalysts have shown promise for the high-throughput and autothermal production of oxygenates (1–4). Partial oxidation of linear C_1–C_5 alkanes over single gauzes has been studied, and it has been found that yields of oxygenates increase with carbon number. This work extends the use of the single-gauze reactor to cyclohexane partial oxidation. Cyclohexane is the lightest cyclic alkane whose C–C bond strength is equal to that of its corresponding linear alkane, and the high symmetry of cyclohexane suggests a small number of possible product species.

The most important commercial reaction of cyclohexane is its liquid-phase oxidation with air in the presence of soluble cobalt catalyst to produce cyclohexanol and cyclohexanone. Cyclohexanol can be converted into adipic acid (for manufacture of Nylon-6,6) with a strong oxidizing agent or dehydrogenated with zinc or copper catalysts to cyclohexanone (5). Cyclohexanone is an intermediate in the production of caprolactam (for manufacture of Nylon-6) as well as adipic acid (6). Conventional technology (7) uses a liquid-phase bubble column or autoclave typically operating at 10 atm, 150°C, and a residence time exceeding 1 h. Selectivities to cyclohexanone and cyclohexanol of 75% can be achieved but only at <5% conversion of cyclohexane.

This paper describes an autothermal method to produce close to 60% selectivity to cyclohexene and the 1,6-difunctionalized oxygenated species 5-hexenal, at 25% cyclohexane conversion and a residence time six orders of magnitude smaller than that for comparable liquid-phase industrial processes.

2. EXPERIMENTAL

2.1. *The Single-Gauze Catalyst*

The catalyst in all experiments was a single 40-mesh (77% transparency) woven gauze with 90% Pt (by mass), 10% Rh, and traces (<10 ppm) of Pd. Alloying Pt with 10% Rh increases the mechanical strength of the wires and reduces Pt losses during high-temperature operation (8). Multiple-layer gauze catalysts woven from fine 90% Pt–10% Rh wire have long been used in the industrial Ostwald process for the partial oxidation of ammonia to produce nitric acid and in the closely related Andrussow process in which a mixture of ammonia, air, and natural gas is converted into hydrocyanic acid (9). This research uses a single layer of the 90% Pt–10% Rh gauze. New gauze catalysts require activation

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before they achieve reproducible results. During the activation process, extensive surface facetting occurs [see, e.g., (4)]. While the nominal wire diameter is initially 76 μm, the wire diameter increases to $\sim$90 μm on catalyst activation.

Species residence times over the catalyst are very short (<1 ms) and mass-transfer rates to and from the catalytic surface are high. It is believed (1–4) that the heat from the exothermic surface reactions along with desorbed free radicals initiate a gas-phase reaction sequence that leads to the formation of unstable oxygenates. The large transparency of the single gauze facilitates rapid mixing of the colder gases passing between the catalyst wires with the hot gases and radicals leaving the gauze surface, resulting in fast quenching of the homogeneous reactions so that oxygenates cannot decompose. Oxygenates are more reactive than alkanes or olefins and are not predicted by equilibrium calculations. Furthermore, oxygenates are not produced significantly from C_5 and C_6 alkanes in Pt-coated foam-monolith reactors (10). The quenching action in the wake region of the single gauze, however, kinetically freezes the product mixture so that valuable nonequilibrium species can be obtained.

2.2. *The Single-Gauze Reactor*

The single-gauze reactor for these experiments consisted of a quartz tube with 19-mm inner diameter and 40-cm length. Two 1-cm-long and 1-mm-thick quartz-tube inserts (15-mm inner diameter) held the gauze in place. The quartz inserts were wrapped with thin Fiberfrax paper (amorphous Al_2O_3–SiO_2 fibers) to prevent bypassing of gases between the insert and the reactor wall and also to ensure rigidity. The reactor was configured vertically and the feed was introduced from the bottom of the reactor. In the region of the catalyst, approximately 1 in. of external insulation was placed around the reactor tube to minimize radial heat losses.

A chromel–alumel thermocouple inside a closed quartz thermowell was used to measure the temperature $\sim$5 mm downstream of the single gauze. The thermowell eliminates the possibility of catalytic chemistry occurring on the chromel–alumel wire. The catalyst surface temperature cannot be directly detected with this probe due to the quartz thermowell which would dissipate heat and interfere with the downstream flow pattern, thus altering the chemistry. Experiments where the 5-mm-downstream temperature was $\sim$500°C corresponded to a surface temperature of $\sim$800°C (measured with a pyrometer), indicating large axial temperature gradients in the wake region of the gauze. The accuracy of the measured downstream temperature was ±5°C.

The flow rates of the high-purity (99.9+%) gases (oxygen, nitrogen, and occasionally *n*-butane for catalyst activation) entering the system from high-pressure cylinders were adjusted using mass-flow controllers which are accurate to ±0.1 SLPM (standard liters per minute) for all gases. Cyclohexane (Aldrich, HPLC-grade 99+% purity) is liquid at room temperature and was introduced as vapor with a syringe pump, fluidized-bed heater, and superheater in series.

The reactor pressure was maintained with a downstream valve and indicated by a standard regulator. For analysis, a valve sending product gas to the gas chromatograph was opened, and the pressure of the reactor and sample lines was adjusted prior to steady-state sampling. Pressures of 1.2 to 2 atm (121.6–202.7 kPa) were possible with the experimental setup. All product gases were incinerated and vented in a fume hood.

2.3. *Catalyst Activation*

To activate a fresh gauze for these experiments, *n*-butane was reacted over the catalyst for $\sim$10 h at $C_4H_{10}/O_2 = 1.4$–2.0 (molar ratio in feed). Activation was confirmed by the reproducibility of temperature, conversion, and selectivities. Activation with cyclohexane alone was not successful after 10 h. All results reported in this paper were obtained with a catalyst fully activated by *n*-butane oxidation. No signs of catalyst deactivation (metal loss, coke formation, etc.) were observed after many hours of reactor operation.

2.4. *Startup and Shutdown*

To light off the gauze catalyst, the cyclohexane flow was first allowed to stabilize in the nitrogen (diluent) flow. Next, oxygen flow was increased until the desired cyclohexane/oxygen ratio was achieved. The gauze catalyst was directly heated until light-off, which occurred at roughly 200–250°C for cyclohexane/oxygen feed ratios (C_6H_{12}/O_2) of 0.4–5.0, respectively. For cases in which the preheat temperature exceeded the ignition temperature, no external ignition source was necessary. At ignition, it was found that the temperature 5 mm downstream increased at a rate of $\sim$10°C/s. The reaction attained steady state within 15 min of ignition, and no significant transients were observed in these experiments after the onset of steady state. The feed ratios were fuel-rich, so the reaction was shut down by stopping oxygen first and then cyclohexane while maintaining the nitrogen flow.

2.5. *Reactor Safety*

Most experiments were performed outside the flammability limits, always on the fuel-rich side. For cyclohexane oxidation, the stoichiometric molar ratio for combustion is $C_6H_{12}/O_2 = 0.11$. In these experiments, the cyclohexane/oxygen ratio was varied between 0.4 and 5.0, never close to the dangerous total-oxidation ratio. The flammability limits in a static system with air are $C_6H_{12}/O_2 = 0.06$–0.44, and flames are generally more favorable for higher pressure, lower dilution, and lower flow rate.

Experiments at $C_6H_{12}/O_2 = 0.4$ with a flow rate of 2.5 SLPM (30% N_2 dilution), preheat temperature of $T_0 = 200°C$, and reactor pressure of $P = 1.2$ atm developed flames originating near the catalyst. The flame velocity was lower than the gas velocity, so the flames extinguished near the reactor entrance. The reactor walls were deposited with solid carbon in this case. At $C_6H_{12}/O_2 = 0.55$, less intense flames emerged but also extinguished. At $C_6H_{12}/O_2 = 0.65$, small pulsing flames were observed steadily shooting upstream of the gauze. These observations were confirmed in several experiments.

Under no reactor conditions did flames develop experimentally when operating at $C_6H_{12}/O_2 > 0.7$. Because most experiments were conducted at $C_6H_{12}/O_2 > 1$ and low pressure, the possibility of dangerous flames or explosions was minimal. In addition to avoiding flames and the possibility of explosions, fuel-rich operation was necessary for significant production of carbon-containing compounds other than CO and CO_2.

2.6. *Product Analysis*

Reaction products were filtered by a 2-μm sintered ceramic element and sent to a Hewlett–Packard 6890 gas chromatograph with a thermal-conductivity detector (TCD). Combining gas chromatography (GC) with mass spectrometry (MS) allowed qualitative determination of several unknown product species. A Finnigan Mat 95 instrument was employed for the GC–MS product analysis. Nitrogen was the calibration gas for mass balances since it was an inert diluent in all experiments. The carbon and hydrogen balances typically closed to within ±5%. All data were reproduced on several catalysts with results consistent with those shown.

The product selectivities were calculated on a carbon-atom basis. Carbon-atom selectivities are calculated as the ratio of the moles of a specific product to the total moles of all products, scaled by the number of carbon atoms in the species. This definition accounts for the mole-number increase due to reaction and satisfies the requirement that all selectivities sum to unity.

Adiabatic reaction temperatures for experimental product distributions were calculated from species enthalpies to be consistent (within ~50°C) with temperatures measured by the thermocouple 5 mm downstream. Although the surface temperatures can greatly exceed these downstream temperatures, the overall energy balance (after hot and colder gases mix) shows that the reactor is nearly adiabatic.

3. RESULTS

3.1. *Effect of Cyclohexane/Oxygen Ratio*

For most partial-oxidation systems, a key parameter is the fuel/oxygen ratio. The cyclohexane/oxygen molar feed ratio C_6H_{12}/O_2 was varied at constant flow rate, dilution, inlet temperature, and reactor pressure. Operating variables of 2.5 SLPM, 30% N_2, $T_0 = 200°C$, and $P = 1.2$ atm (121.6 kPa) promote the production of oxygenates from *n*-pentane (4) and thus should be adequate starting values for cyclohexane. The stoichiometric cyclohexane/oxygen ratio for combustion of cyclohexane to CO_2 and H_2O is 0.11, while the ratio for the partial oxidation to C_6 oxygenates (containing one oxygen atom) or cyclohexene is $C_6H_{12}/O_2 = 2$, approximately 18-fold richer than the combustion ratio. The product distribution for $C_6H_{12}/O_2 = 2$ is summarized in Table 1.

TABLE 1

Product Distribution for Cyclohexane Partial Oxidation at $C_6H_{12}/O_2 = 2.0$, 2.5 SLPM, 30% N_2 Dilution, $T_0 = 200°C$, and $P = 1.2$ atm

Product	% Carbon-atom selectivity
c-C_6H_{10}	31.3
5-$C_6H_{10}O$	25.0
$C_5H_{10}O$	10.3
CO_2	8.5
CO	8.4
c-C_6H_6	4.5
2-$C_6H_{10}O$	2.1
C_2H_4	1.8
CH_3CHO	1.5
C_{7+} oxygenates	1.4
CH_2CHCHO	1.3
C_2H_5CHO	1.0
C_3H_6	0.7
c-$C_6H_{10}O$	0.6
C_4H_8	0.6
C_5H_{10}	0.5

Note. Only significant product species (≥0.5% selectivity) are shown.

Figure 1a indicates the temperature measured 5 mm downstream of the catalyst as well as cyclohexane and oxygen conversions. The temperature ranged widely, from ~700 to ~300°C, as C_6H_{12}/O_2 was varied from 0.65 to 5.0. The drop in temperature was sharp initially but began to level off with high C_6H_{12}/O_2. The curves drawn through the data are intended to be an aid to the eye. Oxygen conversion was ~95% for $C_6H_{12}/O_2 < 1$, but there appears to be an abrupt transition where the O_2 conversion fell to ~85% for $C_6H_{12}/O_2 = 1$, after which it gradually increased to 90% for $C_6H_{12}/O_2 = 3$. For $C_6H_{12}/O_2 > 3$, oxygen conversion decreased drastically and then leveled off at approximately 40%. The transition at $C_6H_{12}/O_2 \approx 1$ was accompanied by a change in the cyclohexane-conversion trend. Dropping sharply until a cyclohexane/oxygen ratio of about unity, the cyclohexane conversion roughly leveled out at ~20% before eventually decreasing to 4% at $C_6H_{12}/O_2 = 5$. Operation beyond $C_6H_{12}/O_2 = 5$ was not possible at a 2.5-SLPM flow rate due to pump limitations. The reaction was nearly

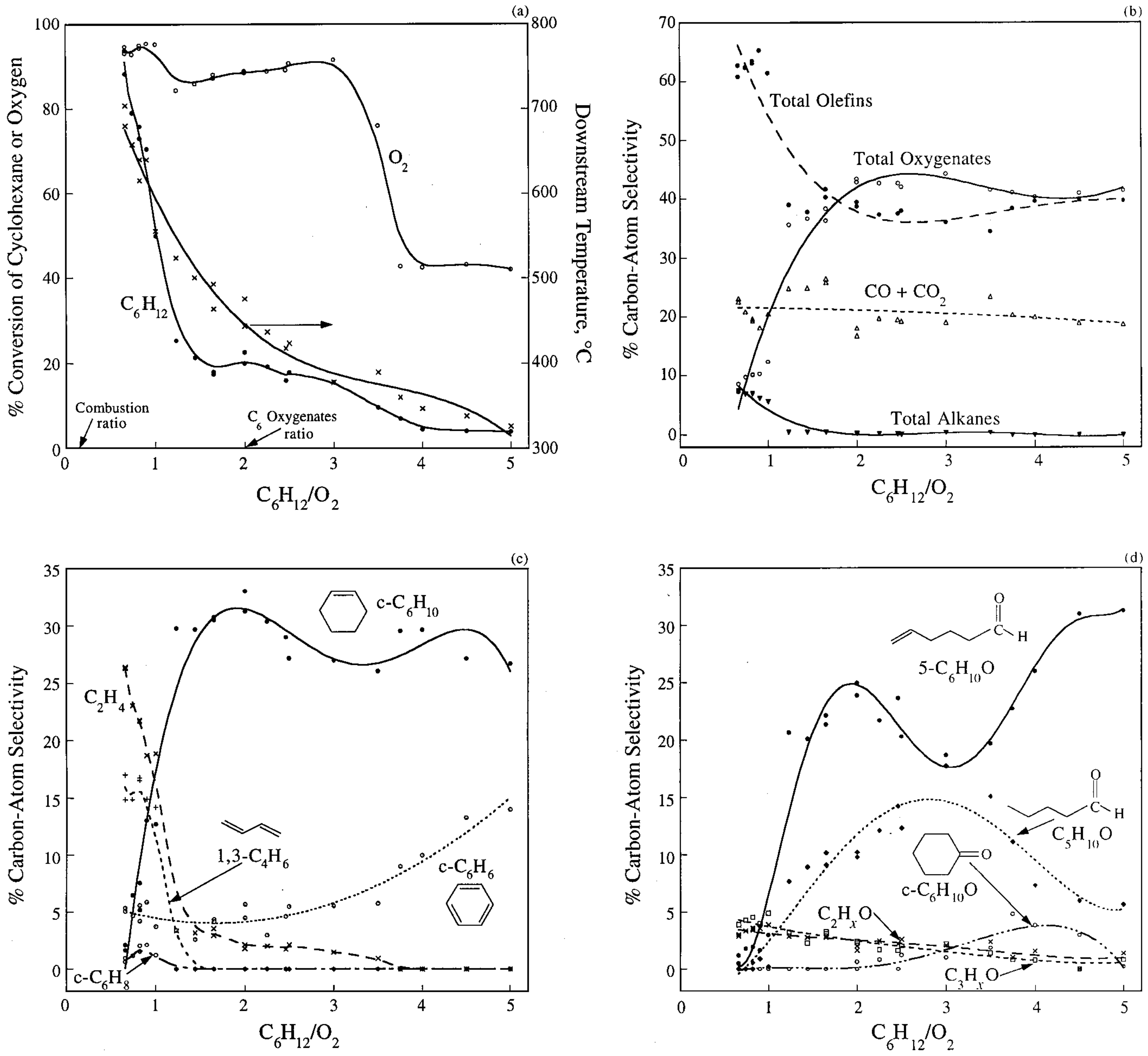

FIG. 1. Effect of cyclohexane/oxygen ratio for 2.5 SPLM, 30% N_2, $T_0 = 200°C$, and $P = 1.2$ atm.

extinguished under these conditions, as indicated by the low temperature and cyclohexane conversion.

Figure 1b shows the overall selectivities (on a carbon-atom basis) to alkanes, CO_x, olefins, and oxygenates. Alkanes were only significant (5–10% selectivity) for $C_6H_{12}/O_2 < 1$. Methane and ethane were the dominant alkanes, although propane, *n*-butane, and *n*-pentane were present in small amounts (<1% selectivity). The selectivity to the total-oxidation products CO and CO_2 was roughly 20% throughout the entire range of cyclohexane concentrations. This result is consistent with the postulate that CO and CO_2 are produced primarily on the catalyst surface. Olefins were very significant (>60% selectivity) for $C_6H_{12}/O_2 < 1$ and were produced with 35–40% selectivity for $C_6H_{12}/O_2 =$ 1–5. Oxygenates, on the other hand, were ~10% selective for $C_6H_{12}/O_2 < 1$ but increased drastically to nearly 45% maximum selectivity at $C_6H_{12}/O_2 = 2.5$. Oxygenates overtook olefins as the dominant product at a cyclohexane/oxygen ratio of about 1.75, and the yield of oxygenates was optimized (at ~10%) for $C_6H_{12}/O_2 \approx 2.0$.

Figure 1c indicates the major individual olefins. For low cyclohexane/oxygen ratios, ethylene and 1,3-butadiene were abundant products, giving evidence of cracking reactions. C_2H_4 and 1,3-C_4H_6 followed the same trends and were both minimal for $C_6H_{12}/O_2 > 1.5$. Propylene (not shown), another cracked product, was >5% selective at low ratios but was not produced for $C_6H_{12}/O_2 > 1.5$. Cyclohexene is an important olefin at all ratios, and it was maximum (>30% selectivity) at $C_6H_{12}/O_2 \approx 2.0$. Benzene was about 5% selective for $C_6H_{12}/O_2 < 3$ and then increased to >10% selectivity for cyclohexane/oxygen ratios exceeding 3. Cyclohexadiene, the intermediate between cyclohexene and benzene, was just a few percent selective at low ratios ($C_6H_{12}/O_2 < 1$) and was not present under richer conditions.

Figure 1d shows the major oxygenates. At low cyclohexane/oxygen ratios ($C_6H_{12}/O_2 < 0.8$), the predominant oxygen-containing species were C_2–C_3 compounds and small amounts of methanol (not shown). C_2H_xO includes acetaldehyde (CH_3CHO) and ethanol (CH_3CH_2OH), and C_3H_xO includes propionaldehyde (CH_3CH_2CHO), propanol (C_3H_7OH), acetone (CH_3COCH_3), and 2-propenal (CH_2CHCHO). For $C_6H_{12}/O_2 > 1$, pentanal ($C_5H_{10}O$) and especially 5-hexenal (5-$C_6H_{10}O$) became the significant oxygenated products. Selectivities of ∼25% to 5-hexenal and ∼15% to pentanal were achieved at cyclohexane/oxygen ratios of 2 and 3, respectively. 5-Hexenal selectivity decreased for cyclohexane/oxygen ratios from 2 to 3 but then increased significantly to >30% for $C_6H_{12}/O_2 = 5$. Cyclohexanone (c-$C_6H_{10}O$) was produced most selectively (∼5%) for $C_6H_{12}/O_2 \approx 4$. The corresponding alcohol, cyclohexanol, was not detected (<0.1% selectivity) in these experiments. Operation at $C_6H_{12}/O_2 = 4$ was desirable in terms of oxygenate formation: 5-hexenal was at least as selective as cyclohexene, and formation of cyclohexanone was optimum. However, cyclohexane and oxygen conversions both suffered at this ratio (Fig. 1a), causing low yields of C_6 oxygenates and high oxygen breakthrough.

3.2. *Effect of Flow Rate*

The total flow rate of reactants passing through the single gauze should affect the surface chemistry because of variation in contact time on the catalyst. In Fig. 2, experimental data are shown for $C_6H_{12}/O_2 = 2.0$, 30% N_2 dilution, $T_0 = 200$°C, and $P = 1.2$ atm. This cyclohexane/oxygen ratio was chosen because it provided the maximum yield of total oxygenates (Fig. 1) and because it is the theoretical stoichiometric ratio for C_6 oxygenates. The total flow rate was varied between 1 and 3 SLPM, which correspond to superficial catalyst contact times of ∼1.0 and ∼0.33 ms, respectively, under these conditions.

Figure 2a shows that oxygen conversion (75–90%) and cyclohexane conversion (∼20%) both increased slightly with flow rate. The downstream temperature fell ∼50°C as the flow rate was varied from 1 to 3 SLPM, perhaps a counterintuitive result because conversions increased and most reactions taking place are exothermic. On the contrary, the surface reactions (such as complete combustion) are more strongly exothermic than are the gas-phase partial-oxidation reactions, by at least an order of magnitude. Higher flow rates translated to lower temperatures because reactant contact times were shorter and less heterogeneous chemistry occurred (compared with homogeneous reactions). The increase in overall conversions with flow rate is consistent with the relative increase in gas-phase chemistry initiated by the catalyst.

If surface chemistry is favored at low flow rates, the selectivity to CO + CO_2 should decrease with flow rate. Indeed, CO_x selectivity fell at least 5% as the flow rate was raised from 1 to 3 SLPM (Fig. 2b). Alkanes were negligible at all flow rates examined. For flow rates <2 SLPM, olefins were favored over oxygenates. Oxygenates surpassed olefins at 2 SLPM, and for a ∼2.5-SLPM flow rate, oxygenates (∼43% selectivity) were more selective than olefins (<40% selectivity) and exhibited a maximum in yield (∼10%). For higher velocities (3 SLPM), olefins slightly increased at the expense of oxygenates, although the effect was small.

Figure 2c shows that the flow rate did not greatly influence cyclohexene selectivity (30–35%). Benzene exhibited a weak decline of a few percent, and cyclohexadiene was not produced. Ethylene increased slightly with flow rate, but 1,3-butadiene was negligible at all flow rates here, so some ethylene must be formed by a pathway different than that which explains the high C_2H_4 + 1,3-C_4H_6 selectivity at low cyclohexane/oxygen ratios (Fig. 1c). Propylene, butylene, and pentene were all <1% selective.

Figure 2d reveals that 5-hexenal may have increased moderately with flow rate, although the scatter suggests that the selectivity was practically constant. Pentanal did increase >5% in selectivity from 1 to 3 SLPM, and the C_2 and C_3 oxygenates were favored somewhat by higher flow rates. Although produced in very small amounts, 2-hexenal followed the same trend as 5-hexenal, indicating similar pathways. Cyclohexanone selectivity was negligible at flow rates from 1 to 3 SLPM under these conditions (in particular, $C_6H_{12}/O_2 = 2$).

3.3. *Effect of Preheat*

The temperature of the feed gases was varied between $T_0 = 100$ and 300°C for $C_6H_{12}/O_2 = 2.0$, 2.5 SLPM, 30% nitrogen dilution, and $P = 1.2$ atm. The experimental results are shown in Fig. 3. Note that T_0 corresponds to the temperature at the catalyst entrance and not the reactor entrance. The normal boiling point of cyclohexane is 81°C so that to avoid cyclohexane condensation the inlet temperature could not be much less than 100°C.

The conversions and catalyst exit temperature (at 5 mm downstream) are plotted in Fig. 3a. The reactor temperature was essentially linear with preheat, increasing ∼100°C for a change in amount of preheat of 200°C. Cyclohexane and oxygen conversions were practically constant at roughly 25 and 90%, respectively. With conversions constant, it could be expected that selectivities also would not be strongly

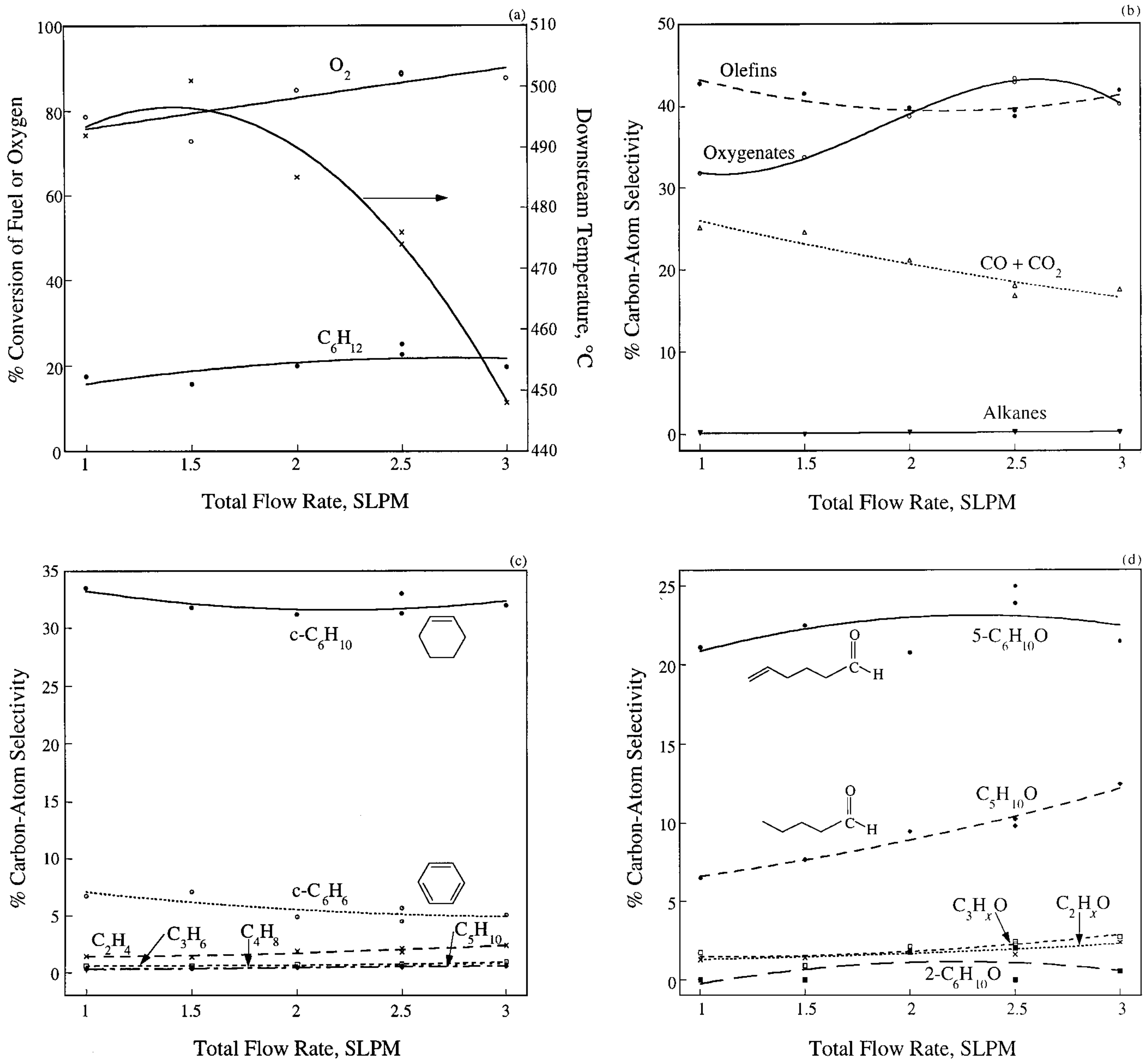

FIG. 2. Effect of flow rate for $C_6H_{12}/O_2 = 2.0$, 30% N_2, $T_0 = 200$°C, and $P = 1.2$ atm.

influenced by preheat. Figure 3b agrees with this assertion. Alkanes were nonsignificant and olefins were ~42% selective for feed temperatures of 100–300°C. Olefin selectivity was enhanced slightly for higher preheat.

Figure 3c shows the major olefins. Cyclohexene was not greatly influenced by preheat, although the data do indicate a weak optimum (>30% selectivity) near $T_0 = 200$°C. All other olefinic species were basically constant except ethylene, which was slightly more abundant at higher inlet temperatures. Figure 3d indicates that the increase in oxygenate selectivity with preheat was due to higher production of 5-hexenal (maximum of ~25% selectivity). C_2H_xO and C_3H_xO were constant, and pentanal decreased with increasing preheat. These opposing trends of $C_5H_{10}O$ and 5-$C_6H_{10}O$ should be considered in any mechanism that attempts to explain the data.

3.4. *Effect of Dilution*

So far, all experiments were performed with 30% nitrogen diluent present. In many reactions, dilution simply lowers the temperature and thus decreases gas-phase reaction rates. In these instances the dilution effect would essentially be the opposite of the preheat effect. However, the single-gauze reactor should be more sensitive to dilution because

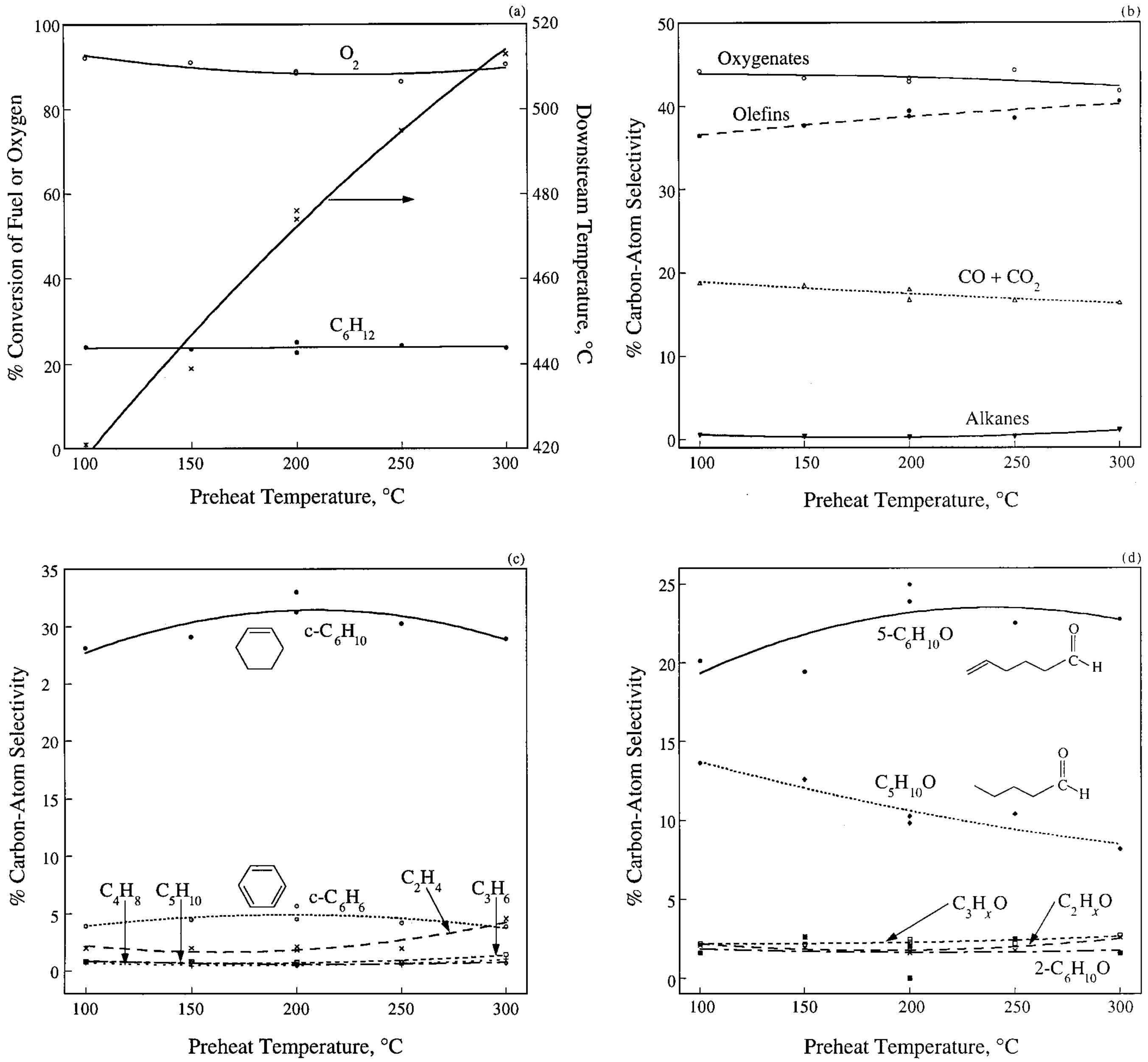

FIG. 3. Effect of preheat for $C_6H_{12}/O_2 = 2.0$, 2.5 SPLM, 30% N_2, and $P = 1.2$ atm.

of the unique quenching effect downstream of the catalyst. In Fig. 4, dilution was varied between 5% (diluent portion of total feed) and 55.6% at $C_6H_{12}/O_2 = 2.0$, 2.5 SLPM, $T_0 = 200°C$, and $P = 1.2$ atm. At this cyclohexane/oxygen ratio, 55.6% N_2 corresponds to an air feed, as noted on the axes. Because some N_2 was needed for GC calibration, a pure-oxygen feed was not tested, but the 5% dilution case should closely resemble reactor operation with pure O_2.

Figure 4a illustrates the temperature and conversions. Temperature, oxygen conversion, and cyclohexane conversion all fell off with increasing diluent concentrations. At low dilution the O_2 conversion was ~95%, but it decreased sharply, falling to <50% with an air feed. The cyclohexane conversion decreased from ~20 to ~10%. In terms of moles converted, the decrease in conversion with dilution was the same for both C_6H_{12} and O_2: about half of the moles were converted in air versus (roughly) pure oxygen.

It may be surprising that the temperature dropped only ~30°C when conversions dropped drastically. As noted previously, the highly exothermic production of CO and CO_2 on the catalyst surface plays a large role in the measured reactor temperature. Figure 4b shows that the CO + CO_2 selectivity increased from 20 to ~40% as dilution was increased from 5 to 56%. In this span the CO_x carbon-atom yield was constant at ~4% with varying dilution. The decrease in reactor temperature must therefore have been

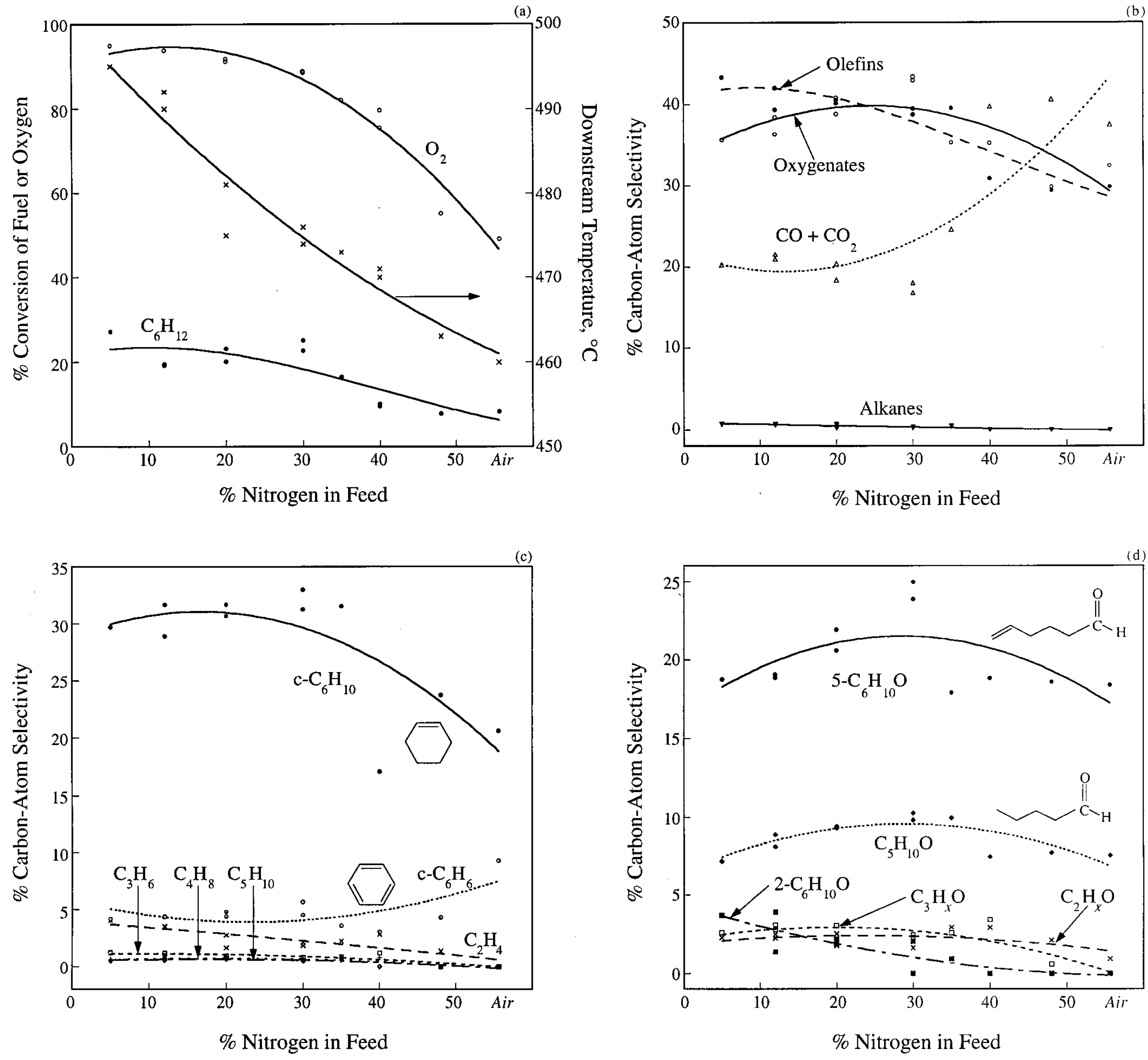

FIG. 4. Effect of dilution for $C_6H_{12}/O_2 = 2.0$, 2.5 SPLM, $T_0 = 200°C$, and $P = 1.2$ atm.

due to lower gas-phase conversion. From Fig. 4b, alkanes were nonsignificant at all nitrogen concentrations. Olefins decreased with dilution, becoming >10% less selective with an air feed. Oxygenates exhibited an optimum in selectivity (~40%) and yield (~8%) at approximately 25% N_2. At this point, oxygenates also overtook olefins as the most selective reaction product, until CO_x dominated at very high dilution when much less homogeneous chemistry occurred.

Cyclohexene (Fig. 4c) basically accounts for the decline in olefin selectivity with increasing dilution, as cyclohexene decreased about 10% in selectivity. Benzene slightly increased and ethylene decreased somewhat. Propylene, butylene, and pentene were not produced significantly, regardless of dilution. The individual oxygenated species are shown in Fig. 4d. C_2 and C_3 oxygenates were most significant for lower dilution. 5-Hexenal and pentanal showed similar trends, contrary to the opposing behavior for varying preheat, emphasizing that dilution and preheat were distinct phenomena for this system. The optima in $C_5H_{10}O$ and 5-$C_6H_{10}O$ were at ~30% N_2, while 2-$C_6H_{10}O$ selectivity was actually maximized (~4%) at the lowest dilution.

3.5. Effect of Pressure

The pressure of the single-gauze reactor was varied between 1.2 and 2 atm for $C_6H_{12}/O_2 = 2.0$, $T_0 = 200°C$, and 30% nitrogen dilution. For these experiments we chose a constant catalyst contact time of 0.7×10^{-3} s. Because superficial contact time decreases linearly with flow rate and increases linearly with pressure, the flow rate was increased as the pressure was raised so that the contact time was maintained at 0.7 ms. The experimental results are shown in Fig. 5.

In principle, higher pressure should cause higher reaction rates in the gas phase. Conversions of cyclohexane and oxygen both increased with pressure, as indicated in Fig. 5a. The cyclohexane conversion increased from <20 to 25%, while the oxygen conversion was enhanced from ~90% at $P = 1.2$ atm to 100% at $P = 2$ atm. The exit temperature increased approximately 20°C throughout this range of pressures.

Figure 5b shows that the selectivity to CO and CO_2 decreased with pressure, suggesting that surface reactions became less important than gas-phase reactions at higher pressure, as expected. As the pressure was raised to 2 atm, the selectivity to oxygenates decreased nearly 5% while the selectivity to olefins increased about 10%. At $P = 2$ atm and the operating conditions indicated, olefins were favored

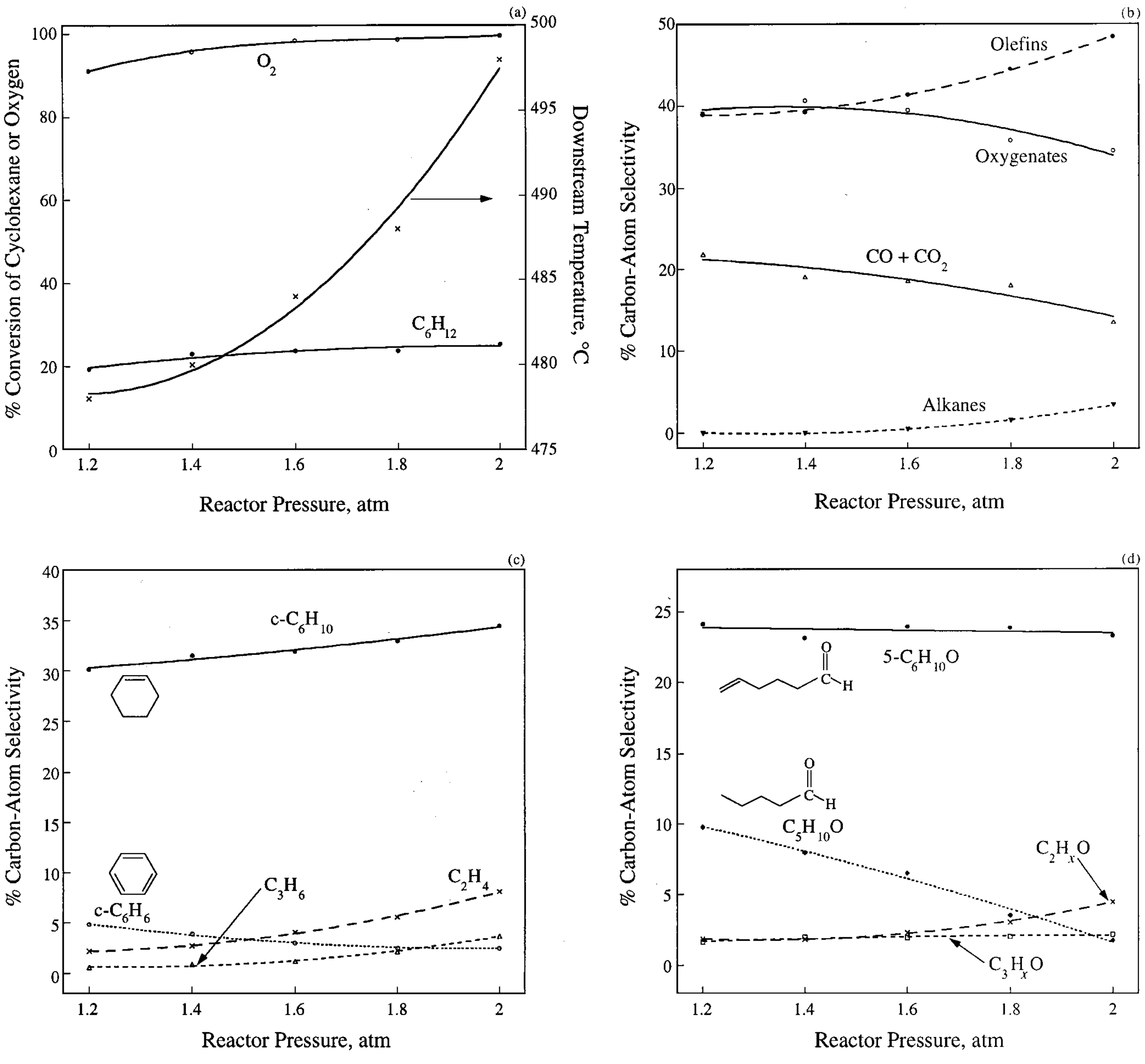

FIG. 5. Effect of pressure for $C_6H_{12}/O_2 = 2.0$, $T_0 = 200°C$, 30% N_2 dilution, and a catalyst contact time of 0.7 ms.

over oxygenates by almost 15% in selectivity. Production of alkanes (mostly ethane) also began to become important at higher pressures. Alkanes are expected predominantly from homogeneous pathways because surface steps should lead to unsaturated products from cyclohexane.

Figures 5c and 5d present the influence of pressure on the selectivities to individual olefins and oxygenates, respectively. Cyclohexene, ethylene, and propylene selectivities increased with reactor pressure, while benzene production was cut in half as the pressure was raised to 2 atm. The trend in benzene resembles the trend in CO_x formation, suggesting that benzene may be a surface-generated species. The selectivity to 5-hexenal (Fig. 5d) does not appear to be greatly influenced by the pressure. The decrease in oxygenates was due mainly to a decrease in the production of pentanal, which declined in selectivity from 10% at 1.2 atm to <2% at 2.0 atm. At $P = 2$ atm, the selectivity to 5-hexenal and cyclohexene was ∼58%.

4. DISCUSSION

4.1. *Overall Process*

The cyclohexane/oxygen ratio was the most important variable for operation of the single-gauze reactor, as seen in Fig. 1. Temperatures, reactant conversions, and product selectivities all changed significantly as C_6H_{12}/O_2 was varied from 0.65 to 5.0. Oxygenates were produced at >40% selectivity for $C_6H_{12}/O_2 \geq 2$. Nearly 70% selectivity to three particular products—5-hexenal, pentanal, and cyclohexene—could be achieved with this single-gauze reactor. Cyclohexanone was made with 5% selectivity at $C_6H_{12}/O_2 \approx 4$, although oxygen and cyclohexane conversions were both relatively low.

The flow rate (or contact time) of reactant gases (Fig. 2) was somewhat important. Oxygenates were favored by higher flow rates, showing an optimum in selectivity at roughly 2.5 SLPM for the range examined. From Fig. 3, the effect of preheat was smaller and different than that of dilution. Selective production of oxygenates over olefins was promoted by lower inlet temperatures. Small amounts of nitrogen diluent (<10% N_2) favored olefin production, while high dilution (>40% N_2) suppressed the homogeneous reactions necessary for oxygenate formation (Fig. 4). The constant yield (∼4%) of $CO + CO_2$ suggests that the surface chemistry was largely unaffected by dilution. A reactor pressure of 2 atm (Fig. 5) promoted higher yields of the C_6 products cyclohexene and 5-hexenal while decreasing the formation of pentanal.

4.2. *Reaction Mechanism*

Although a full explanation of the data requires both heterogeneous and homogeneous mechanisms, the formation of the major species is hypothesized to occur in the gas phase once the reaction is heterogeneously initiated. Figure 6 shows a simplified surface-assisted homogeneous reaction scheme consistent with the major species observed experimentally.

The initial step is H-atom abstraction of cyclohexane to form the cyclohexyl radical. This step can occur oxidatively whereby an oxygen molecule reacts directly with cyclohexane and strips off a hydrogen atom, forming $HOO\cdot$ and $C_6H_{11}\cdot$. Alternatively, a radical $R\cdot$ (e.g., $C_4H_7\cdot$ or $OH\cdot$) desorbing from the gauze surface into the gas phase could collide with cyclohexane and abstract H, forming RH and $C_6H_{11}\cdot$. The direct reaction with O_2 has a large activation energy, although the intense heat provided by the surface reactions could help overcome the energy barrier for the oxidative step. Because the system is lean in oxygen, the radical-assisted initiation step is likely to be as important as the oxidative route for abstracting a hydrogen atom. Furthermore, plug-flow calculations using a homogeneous-only reaction mechanism (11) with >150 species and ∼3000 reactions suggest that surface generation of radicals is necessary to account for the experimental cyclohexane conversions at millisecond time scales.

The cyclohexyl radical can dehydrogenate oxidatively to form cyclohexene, undergo β-decomposition reactions to form smaller products (especially at higher temperatures), or directly add an oxygen molecule to form the important cyclohexylperoxy radical $C_6H_{11}OO\cdot$.

The cyclohexylperoxy radical can go to cyclohexene by loss of $HOO\cdot$, but it can also rearrange by a back-biting reaction in which the radical abstracts an internal H atom. The abstraction generally occurs at least two carbons away from the site of the peroxy radical. The cyclohexylperoxy radical should closely follow this rule due to the close proximity of the peroxy group (at the α position) with the two axial γ-H atoms which are therefore more readily abstracted. Interactions with α-, β-, and especially δ-H atoms are not spatially preferred. The $\cdot C_6H_{10}OOH$ species with the free radical γ to the peroxy carbon should be the favored cyclohexylperoxy isomer, as depicted in Fig. 6.

Loss of a hydroxy radical from γ-$C_6H_{10}OOH\cdot$, which should occur with low activation energy (12), leads to a species that strongly favors ring rupture and the formation of the olefinic aldehyde 5-hexenal. If γ-$C_6H_{10}OOH\cdot$ instead ejects a formyl radical ($CHO\cdot$), pentanal is produced. The data in Fig. 1d suggest a competition between these C_5 and C_6 oxygenates, consistent with the parallel consumption of γ-$C_6H_{10}OOH\cdot$ hypothesized in Fig. 6.

Within this scheme, cyclohexanone formation should not be favored because it requires the cyclohexylperoxy radical with the unpaired electron on the peroxy carbon. Rearrangement to this isomer from the originally formed $C_6H_{11}OO\cdot$ species is spatially difficult, as it requires interaction of the axial peroxy group with the equatorial

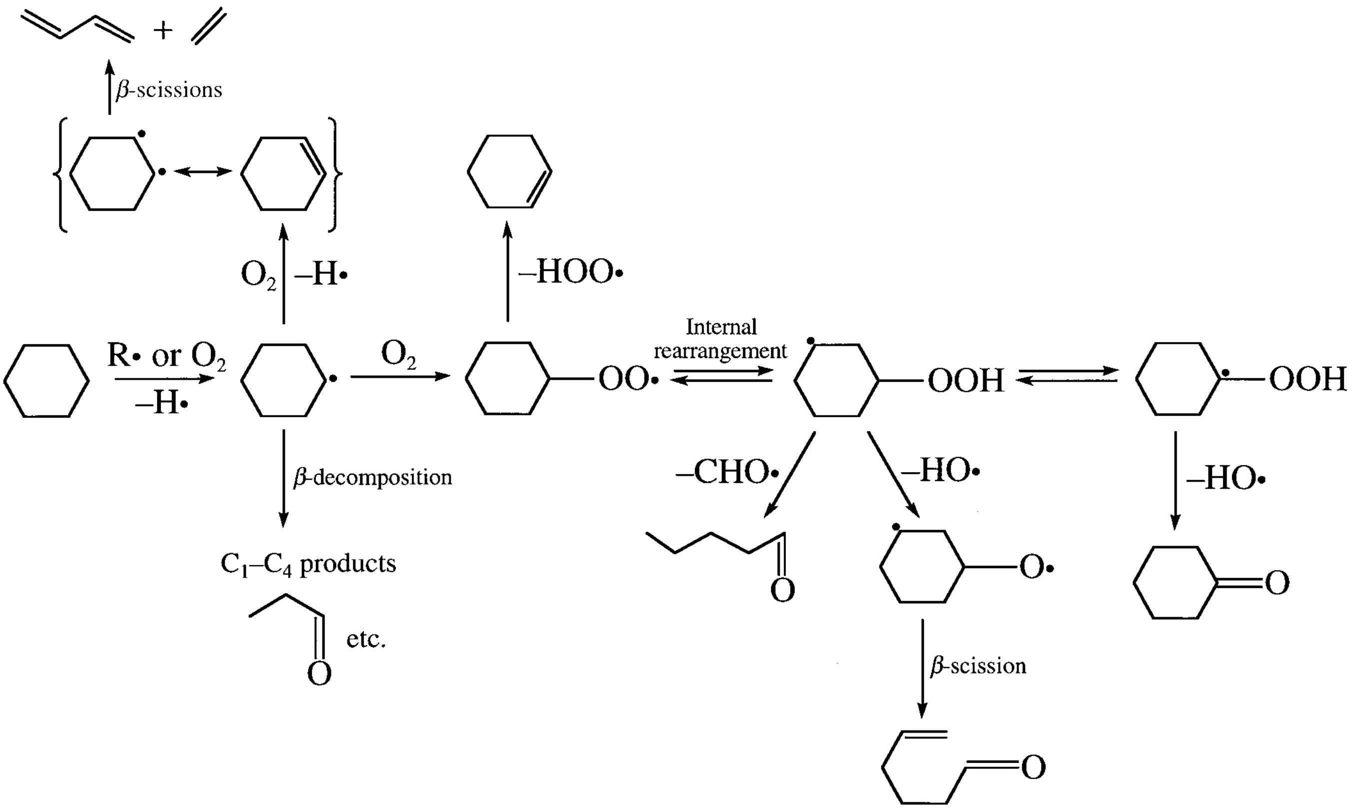

FIG. 6. Proposed surface-assisted homogeneous reaction pathways for cyclohexane partial oxidation.

α-hydrogen. The ∼5% maximum selectivity to cyclohexanone was apparently made possible by internal abstraction of the α-hydrogen with transfer of a radical from the γ-carbon to the α-carbon, as indicated in Fig. 6. There may be alternate pathways; Figure 6 is just one possibility and probably a partial explanation at best.

The high selectivities of cyclohexene over wide ranges in conditions are consistent with the proposed mechanism. The decline in cyclohexene selectivity with dilution (Fig. 4c) suggests predominantly gas-phase production of cyclohexene. Benzene, which along with CO_x is predicted by equilibrium at the high temperatures on the surface, must proceed through cyclohexene. Benzene is probably produced by both heterogeneous and homogeneous reactions. Desorption from the catalyst after a single dehydrogenation is unfavorable, implying that most of the cyclohexene is a gas-phase product. It is attractive that while benzene is a thermodynamic sink for the oxidative dehydrogenation of cyclohexane, the cyclohexene/benzene production ratio was typically >5 in these experiments.

For higher temperatures (lower cyclohexane/oxygen ratios), large amounts of ethylene and 1,3-butadiene resulted from cracking reactions. One mechanistic possibility is that cyclohexene (which is equivalent to cyclohexane with adjacent free radicals) undergoes a double β-scission, rupturing the 3,4 and 5,6 C–C bonds. This concerted reaction would indeed produce 1,3-C_4H_6 + C_2H_4, as drawn in the scheme in Fig. 6. Some ethylene is formed by another pathway (Figs. 1–5), perhaps through cyclohexyl β-decompositions (on the surface or in the gas phase).

To address potential arguments that the entire process is strictly homogeneous, the Pt–10% Rh catalyst must be lit off for the single-gauze reactor to produce valuable species. Experiments at $C_6H_{12}/O_2 = 2$, 2.5 SLPM, 30% N_2, $T_0 = 200$°C, and $P = 1.2$ atm but without catalyst ignition showed absolutely no reaction. The presence of an unignited gauze would interfere with gas-phase reactions if free radicals were terminated on the surface. Experiments with an empty tube (no catalyst present) heated to 200°C also showed no reaction, verifying that the essential reactions here require an ignited catalyst.

5. CONCLUSIONS

Coupled heterogeneous and homogeneous chemistry using a 90% Pt–10% Rh single-gauze catalyst allows the selective production of nonequilibrium species from the partial oxidation of cyclohexane. A portion of the cyclohexane feed reacts completely on the surface, generating heat and free radicals which initiate a gas-phase reaction sequence. The homogeneous chain reactions that produce desired oxygenated hydrocarbons and olefins are then thermally quenched by cold gases passing between the wires. Much higher selectivities to oxygenates can be achieved with a Pt–10% Rh single gauze versus a Pt-coated foam monolith which does not permit quenching.

Two main regimes of operation exist, with a transition near a cyclohexane/oxygen ratio of unity. Lean operation ($C_6H_{12}/O_2 < 1$) allows >60% selectivity to olefins (mostly cyclohexene, 1,3-butadiene, and ethylene). For richer operation ($C_6H_{12}/O_2 > 1$), 5-hexenal, cyclohexene, and pentanal dominate, with ∼70% maximum selectivity to these three products. A reactor pressure of 2 atm is desirable because it inhibits the formation of CO_x and pentanal and increases reactant conversions. The reactor is able to produce oxygenates at selectivities exceeding 40% for $C_6H_{12}/O_2 \geq 2$, with a maximum oxygenate yield at $C_6H_{12}/O_2 \approx 2$. Total selectivities of ∼85% to oxygenates and olefins (including ∼60% to the two C_6 products, cyclohexene and 5-hexenal) are attainable at ∼25% cyclohexane conversion and 100% oxygen conversion. Cyclohexanone can be produced with 5% selectivity at very high cyclohexane/oxygen ratios ($C_6H_{12}/O_2 \approx 4$).

Our single-stage autothermal reactor can process ∼8 kg/day cyclohexane and produce 5-hexenal and cyclohexene with carbon yields of ∼0.55 and ∼0.65 kg/day, respectively, at a pressure of 2 atm. Direct scaleup to a reactor with a gauze of 1-m diameter at constant contact time and no recycle should give ∼5400 kg/day (6 tons/day) of a mixture of 5-hexenal and cyclohexene. Such a blend could potentially be useful for the manufacture of nylons or other polymers. The main economic hurdle for this technology is presumably that separation of the product stream would be energy-intensive.

Efforts are underway to computationally model the single-gauze reactor using detailed chemistry for the production of oxygenates and olefins from the partial oxidation of cyclohexane. Numerical simulations will aid in further understanding the surface-assisted gas-phase process and should help adjust reactor operation for desired product distributions.

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