Dehydrogenation of Pentanes with Oxygen

CHARLES M. SELWITZ and JOSEPH L. STANMYER, Jr.
Gulf Research and Development Co., Pittsburgh Pa.

Studies were made on the dehydrogenation of normal and isopentane with oxygen (in air) to obtain olefins of the same skeleton as the parent paraffin. Oxygen acts as a dehydrogenation agent at low concentrations and the main reaction is essentially complete within the first second. Efficiency of isopentene formation declines steadily with increasing temperature from 350° C. where a 43% selectivity and a 15% conversion were obtained in a stainless steel reactor. Conversion passed through a maximum (26%) at 400° C. The reactivity and conversion of normal pentane were greater than that of isopentane but selectivity to olefin was less. Ozone did not greatly increase conversion but did severly cut olefin selectivity at lower temperatures. Metallic, radical-destroying surfaces gave lower conversions and higher olefin selectivities than inert surfaces. Pentanes are too reactive to be converted to pentenes in good yield.

BELOW 400° C., the homogeneous vapor phase reaction of paraffins with approximately equimolar amounts of oxygen is known to produce predominantly oxygenated products; above 500° C., lower molecular weight paraffins and unsaturated hydrocarbons are formed by cracking reactions (*6*). Between these two ranges, the temperature coefficient is negative, i.e., the amounts of paraffin reacted decreases with increase in temperature. This is indicative of a change in reaction mechanisms (*7*). Also in this intermediate range, dehydrogenation to olefins of the same skeletal structure:

$$2\,R{-}CH_2{-}CH_2{-}R' + O_2 \rightarrow 2\,RCH{=}CH\,R' + 2\,H_2O$$

takes place with relatively high efficiency. The dehydrogenation with oxygen of the smaller hydrocarbons, ethane and propane, in particular has been extensively studied (*2, 8*). The similar dehydrogenation of larger paraffins is less attractive for a number of reasons (*5*), but with the growing demand for unsaturates it was decided to evaluate this route to high olefins. In particular, the interest in isoprene made it desirable to study the dehydrogenation of isopentane. The reaction of both normal pentane and isopentane with sufficient air to maintain a 2 to 1 hydrocarbon to oxygen ratio was studied between 300° and 500° C. The effects of residence time, temperature, surface, and small amounts of ozone on paraffin conversion, olefin selectivity (moles of olefin per mole of paraffin reacted) and product distribution were determined in order to find the optimum conditions for this reaction.

EXPERIMENTAL

Both the normal pentane and isopentane charge stock were 99% purity.

The proper air-hydrocarbon mixture was obtained by passing air under controlled flow conditions through Drierite and then through a carburetor containing the hydrocarbon in a constant temperature bath maintained at a temperature to give the desired hydrocarbon to oxygen ratio of 2:1. The hydrocarbon saturated air stream was then passed through a flashback chamber and into the reactor. Reactors were constructed of iron, stainless steel and Vycor and all were very similar in dimensions. They were 36 inches long and each contained a thermowell. The tubes were heated over 25 inches by three circuits of resistance wire and were kept within ±3° of the desired run temperature. The internal volume of the reactor was 180 cc. Each reactor contained five take-off valves located 5 inches apart along the length of the reactor. Thus, for any given rate of air flow, five different residence times were obtainable at 20, 40, 60, 80, and 100% of the maximum residence time. A control valve was placed at the exit end of the reactor and all runs were made at a pressure of 836 mm. of Hg. The bulk of the work was done with isopentane and the stainless steel reactor, although a lesser number of runs with this hydrocarbon were made in the iron reactor coated with B_2O_3, and with the Vycor reactor which was either washed with HF before each run, or coated with a silver mirror. Normal pentane oxidation was studied over the latter two surfaces only.

Runs in which catalytic amounts of ozone were added were made by splitting the air stream, passing exactly one half through the carburetor at an elevated temperature, passing the other half through a Welsbach T-23 Ozonizer and then remixing the two streams at the entrance to the reactor. Ozone analysis was carried out at this point by a Welsbach Ozone Meter, Model C.

Analysis was obtained from gas samples taken just after the carburetor and just after take-off valves. The exit stream was subsequently passed through a calibrated dry test meter and then into traps where liquid product was accumulated. Since the primary concern was with isopentene production, analysis was concentrated on the use of vapor chromatography for the determination of pentane conversion, pentene selectivity and the distribution of the pentene isomers. In addition, mass spectrographic analysis of the gas samples made possible determination of hydrogen, CO, CO_2, and light hydrocarbons. The amount of water was obtained by subtracting from the liquid product formaldehyde, acetaldehyde and acid (as acetic acid) which were determined in this phase by standard techniques. Condensed polymeric material, and other water soluble compounds, particularly methanol, were also formed. Attempts to detect peroxide in the product were unsuccessful.

RESULTS

Dehydrogenation of Isopentane with Oxygen. Effect of Temperature. Experiments were conducted at 50° intervals from 300° to 500° C. in a stainless steel reactor. In this system, run at a ratio of nitrogen:isopentane:oxygen of 4:2:1, reaction of isopentane was essentially complete within the first second. The hydrocarbon conversion increased very sharply above 300° C., passed through a maximum around 400° C., and then decreased in the negative temperature coefficient range, Figure 1. A maximum conversion of 26% with an isopentene selectivity of 31% occurred at 400° C. The isopentene selectivity declined steadily from the lowest temperature at which a significant conversion occurred, i.e., 350° where a 43% selectivity and a 15% conversion were obtained. At the lowest temperature studied, 300° C., the number of moles of water formed per mole of isopentane reacted was almost unity, 1.03 but this rose with temperature to a value of 1.8 at 500° C., Figure 2. An increase in CO_2 and light hydrocarbons, and a decrease in CO and aldehydes occurred as the run temperature was increased through this region of changing reaction mechanisms.

Effect of Residence Time. The dehydrogenation of isopentane to olefins appears to be complete for the most part within the first second. Thereafter isopentane conversion increases slightly and isopentene selectivity is almost constant with time. This is illustrated in Figure 3, where the results of runs in a stainless steel and a boric oxide coated iron reactor are compared. Much of the reaction between 1 and 5 seconds is a result of secondary interactions among the products initially formed. The increase in oxygen utilization and oxidation products, e.g., water, CO_2, aldehydes, indicates this. Figure 4 demonstrates the occurrence of another secondary reaction. This terminal methylbutenes, 3-methylbutene-1 and 2-methylbutene-1, form 80% of the initial isopentene product. 3-Methylbutene-1 is relatively stable and declines only slightly with time but the percentage of 2-methylbutene-1 falls off sharply while the internal isomer, 2-methylbutene-2, increases considerably with time. Therefore the branched terminal double bond appears to isomerize under these conditions much more readily than similar unsaturation which is not branched.

Effect of Ozone. When small amounts of ozone (0.1 to 0.5 mg./liter) were added to the reaction stream, the picture became somewhat altered, Figure 5. Reaction initiating radicals formed by the decomposition of the ozone, would be expected to give a considerable increase in conversion in the region of highest olefin selectivity. Although the conversion was increased slightly at 300° C., it was actually lowered between 350° and 400° C. The negative temperature effect was either eliminated or displaced to a much higher temperature. There was unexpectedly a complete reversal of the lower temperature portion of the isopentene selectivity curve. Above 400° C. the two curves tend to coincide.

Effect of Surface. The effect of the four surfaces studied on conversion and selectivity is shown in Table I for experiments made at 400° C. and 4–5 seconds residence time. The hydrofluoric-acid-washed-Vycor represents the surface most inert towards chain branching radicals such as the hydroxyl radical while silver represents the surface most destructive to free radicals (*3*). Thus the series in the table qualitatively represents a range of increasing reactivity. The results over the silvered surface are the least reliable inasmuch as only two experiments were performed and the silver mirror visibly deteriorated during the course of the run. The difference in performance between the various surfaces is not large, even between runs made over Vycor and silver. However, the shift in results on a per-mole-reacted-basis is consistent with the changing nature of the surface. As we go from a surface with no tendency to destroy free radicals, i.e., Vycor, to one with maximum reactivity toward radicals the conversion drops, olefin efficiency rises, aldehyde and CO formation decrease while CO_2 production increases. The formation of water is somewhat irregular but appears to decrease.

Since the oxygen utilization continues after there is no further dehydrogenation, Figure 3, the change in oxygenated products more accurately represents the effect of nature of the surface on the secondary reactions rather than on the primary reactions.

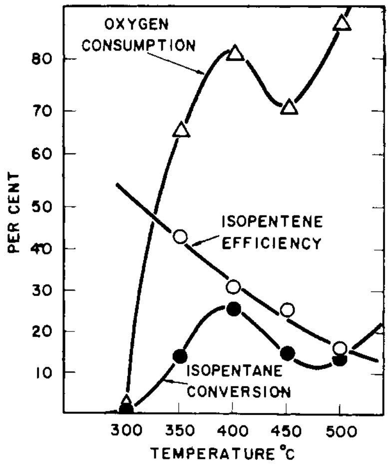

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Figure 1. Effect of temperature on reactants and isopentene formation during isopentane oxidation

(Residence time = 5 seconds)

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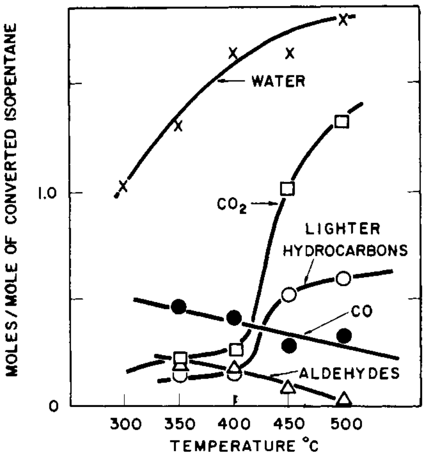
Figure 2. Effect of temperature on by-product formation during isopentane oxidation

(Residence time = 5 seconds)



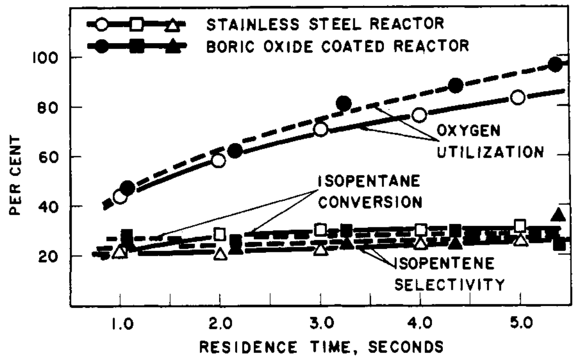


Figure 3. Effect of residence time on isopentane oxidation 400° C.

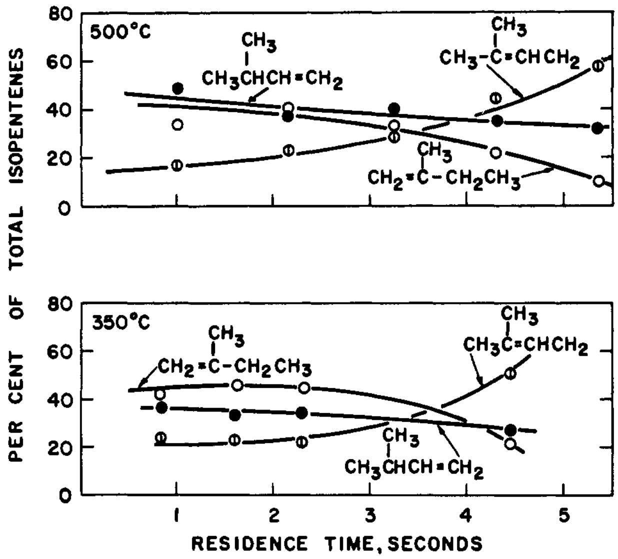


Figure 4. Effect of residence time on isopentene distribution

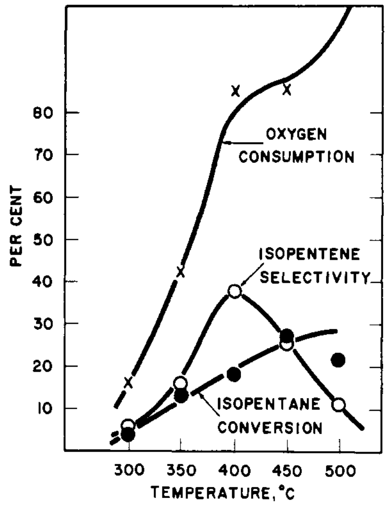


Figure 5. Effect of temperature on isopentane oxidation catalyzed by ozone
(Residence time = 5 seconds)

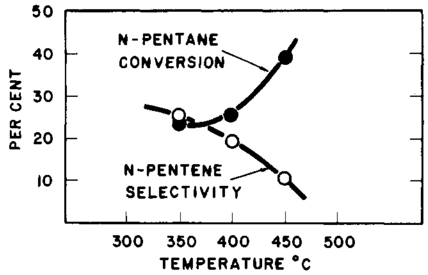


Figure 6. Effect of temperature on pentane conversion and pentene formation during *n*-pentane oxidation
(Residence time = 5 seconds)

Dehydrogenation of Normal Pentane with Oxygen. A limited number of experiments was conducted with normal pentane at 350°, 400°, and 450° C. over Vycor and at 400° C. over silver. The temperature effect in the Vycor reactor is shown in Figure 6. The selectivity to olefin appears to fall sharply with rising temperature. This is similar to isopentane dehydrogenation in the stainless steel reactor. The *n*-pentane conversion curve does not show a negative temperature coefficient in this range. In general, the effects of residence time, ozone, and surface on the two paraffins are similar. The normal pentane is the more reactive isomer and tends to give higher conversion, and oxygen utilization but lower olefin yields. Table II illustrates this and the fact that differences are greater over the radical destroying silver surface than over the inert Vycor surface. Pentene isomer distribution is given in Table III. Over the range of temperatures and contact times studied there is almost no double bond migration and no skelatal isomerization; only *n*-pentenes are formed. The pentene distribution [at 358° to 366° C. the equilibrium mixture would contain 85% pentene-2 and 15% pentene-1 (*4*)] is: pentene-1, 31.1 ± 1.1%; *cis*-pentene-2, 25.0 ± 0.5%; *trans*-pentene-2, 43.8 ± 0.8%. This supports the observation made with the isopentenes that there is little tendency of unbranched double bonds to migrate under these conditions.

DISCUSSION

The results indicate that oxygen does act as a dehydrogenating agent at low concentrations and that this dehydrogenation goes by a mechanism similar to that suggested by Appleby (*1*) for butane oxidation:

$$C_5H_{12} + O_2 \rightarrow C_5H_{11}^* + HO_2^* \qquad (1)$$

$$C_5H_{11}^* + O_2 \rightarrow C_5H_{10} + HO_2^* \qquad (2)$$

$$C_5H_{12} + HO_2^* \rightarrow C_5H_{11}^* + H_2O_2 \qquad (3)$$

$$H_2O_2 \xrightarrow{\text{Surface}} H_2O + \tfrac{1}{2}O_2 \qquad (4)$$

$$2HO_2^* \xrightarrow{\text{Surface}} H_2O + 1\tfrac{1}{2}O_2 \qquad (5)$$

$$C_5H_{11}^* \rightarrow CH_3^* + C_4H_8 \qquad (6)$$

$$CH_3^* + C_5H_{12} \rightarrow C_5H_{11}^* + CH_4 \qquad (7)$$

$$C_5H_{11}^* \rightarrow C_2H_4 + C_3H_7^* \qquad (8)$$

$$C_3H_7^* + C_5H_{12} \rightarrow C_3H_8 + C_5H_{11}^* \qquad (9)$$

$$C_5H_{11}^* + HO_2^* \rightarrow C_5H_{11}O_2H \rightarrow \text{Oxygenated by-products} \qquad (10)$$

At low conversions, olefin selectivities are high, the molar ratio of water to reacted pentane is about unity, and 80 to 90% of the reacted oxygen goes to water. The light

Table I. Effect of Surface on Isopentane Dehydrogenation at 400° C.

						Moles Per 100 Moles of Reacted Isopentane					
Surface	No. of Expt.	Isopentane Conversion %	Isopentene Selectivity	Oxygen Selectivity	Residence Time Sec.	CO	CO_2	Light Hydrocarbons	Water	Aldehydes	Acids
Vycor	4	30.6±1.5	25.2±1.2	8.3	4.8	39	1	17	2.42	27	1
B_2O_3	4	28.0±0.5	28.8±1.2	8.9	4.3	48	6	23	2.74	10	1
Stainless Steel	8	25.8±0.6	30.8±1.6	9.4	5.0	41	26	15	1.63	19	1
Silver	2	17.7±0.5	34.8±2.4	8.3	4.4	16	26	8	1.87	9	0

Table II. Comparison of the Dehydrogenation of Isopentane and Normal Pentane with Oxygen

Compound	Surface	Residence Time, Secs.	Hydrocarbon Conversion	Olefin Selectivity	Oxygen Conversion
n-Pentane	Silver	4.3	24.2	24.0	98.1
Isopentane	Silver	4.3	17.8	34.8	74.6
n-Pentane	Vycor	4.5	29.7	18.7	99.7
Isopentane	Vycor	4.8	30.6	25.2	92.8

Table III. Pentene Isomer Distribution for Normal Pentane Oxidations

Temp. ° C.	Pentene-1	Residence Time, Sec.	*Cis*-Pentene-2	*Trans*-Pentene-2
350	0.9	31.2	25.3	43.6
350	4.3	29.9	25.2	44.8
400	1.0	30.6	25.6	43.7
400	2.4	30.7	24.6	44.7
450	4.5	33.6	24.4	42.0

hydrocarbons consist almost entirely of methane, ethylene, propane, and butenes. The effect of surface is less than might be expected but this probably is due to the high nitrogen concentration which acts as an inert diluent and hinders wall reaction. However, the surface effect, though small, is very definite. Those surfaces which destroy radicals and prevent degenerate branching give the lowest conversions and the best olefin efficiencies. Our results with ozone are in agreement with those of Schubert and Pease (*9*) who showed that ozone at low concentrations has sufficient half life at 300° to 400° C. to effect the oxidation and that it initiates to a limited degree oxidation of lower paraffins at temperatures below the normal range. The suppression of olefin formation, which was not noted in their work, might be explained by an initiation reaction involving ozone.

$$RH + O_3 \rightarrow RO^* + HO_2 \qquad (11)$$

which is competitive with Reaction 1 but is more likely to lead to oxygenated derivatives rather than olefins. In general, the reactivity and conversion of isopentane were less than that of normal pentane while the olefin selectivity was greater. Although reaction is favored at the *tert*-hydrogen-carbon bond the initial abstraction of a hydrogen atom from the hydrocarbon molecule is not the slowest step in the propagation of reactive chains. [The greater stability of the *tert*-amyl radical gives it a life longer than that of the secondary pentyl radical, in the search for a reactive species which will remove the hydrogen from an adjacent carbon.] The dehydrogenation is favored in temperatures below the range of the negative temperature coefficient and the best efficiencies were obtained by operating in a metal reactor without diluent at low residence time and conversion. The pentyl radicals cleave too readily, and react with oxygen, and thus the five-carbon paraffins are excessively reactive and can not be converted to pentenes in sufficient yield to make this route to the olefins practical.

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