

Controlled Combustion Reactions of Light Hydrocarbons

JENNINGS H. JONES, H. DONALD ALLENDORF, DAVID G. HUTTON, and MERRELL R. FENSKE
Petroleum Refining Laboratory, The Pennsylvania State University, University Park, Pa.

HIGHLY EXOTHERMIC vapor phase oxidation reactions are easily controlled by conducting them in the presence of a "rain" of solids which removes reaction heat and prevents combustion. With the proper choice of conditions and solids flow rates, temperatures of hydrocarbon-oxygen reaction mixtures can be maintained within a 5° to 10° C. range. The amount of solids needed for good temperature control occupies only a small proportion (less than 1% by volume) of the reaction zone and thus allows reaction to occur in what is essentially an open tube.

Previous work (2) demonstrated the usefulness of a rain of solids in oxidizing hexane and higher hydrocarbons; this article describes results obtained with a number of light hydrocarbons.

APPARATUS

The oxidation apparatus has been described (2). The solids circulated for heat removal consisted of fused zircon silica (The Carborundum Co.) about 300 microns in diameter. Either oxygen or air was used as the oxidant, equally distributed through four separate inlets along the length of the reaction zone.

EXPERIMENTAL RESULTS

The experiments reported were merely of an exploratory nature, to determine the major products formed from a number of different feedstocks under a variety of conditions; no attempt was made to determine the optimum conditions for producing any single product or type of products.

The quantity of hydrocarbons subjected to oxidation in the various experiments varied from about 200 to 1000 grams. Material balances varied from 90 to 97%; however, to express the results on a uniform basis, all data were calculated using carbon and oxygen balances based on the quantities of products actually found.

Source of Materials. The purities or compositions indicated are based on gas chromatographic analyses made in this laboratory. *n*-Butane (99.7+%), isobutane (99.5+%), 1-butene (88.9% 1-butene and 11.1% 2-butenes), and 2-butenes (99.7%), all Phillips Petroleum Co. pure grade. Propane (99.6%), The Matheson Co. c.p. grade. Isobutene (98.1% isobutene, 1.2% 2-butenes, and 0.7% isobutane), this laboratory.

Product Analyses. The products of the oxidations consisted of noncondensable gas, hydrocarbon-rich material condensed in dry ice-acetone-cooled traps, and an aqueous layer containing the major proportion of the oxygenated compounds produced in the reaction. Gas chromatographic procedures were used extensively in the analytical work. The instrument was a Perkin-Elmer Model 154C unit.

NONCONDENSABLE GAS. Hydrogen, oxygen, nitrogen, carbon monoxide, and methane were determined using a 20-foot length of 1/4-inch tubing packed with Linde Molecular Sieves, Type 5A, while operating at 100° C. and a helium flow rate of 40 ml. per minute. Hydrocarbons (C₂ to C₆) and carbon dioxide were determined using a 27-foot length of 1/4-inch tubing packed with HMPA (hexamethylphosphoramide) on Chromosorb while operating at 30° C. and a helium flow rate of 50 ml. per minute.

With this substrate ethane and ethylene appeared together as a single peak. (Isobutene and 1-butene also gave a single peak.) The ethane-ethylene separation was resolved using a 7 1/2-foot column packed with Linde Molecular Sieves, Type 13X, while operating at 100° C. and a helium flow rate of 125 ml. per minute.

HYDROCARBON-RICH PRODUCT CONDENSED IN DRY ICE-ACETONE-COOLED TRAPS. Hydrocarbons were determined using the HMPA column at 30° C. Oxygenated compounds and proportion of total hydrocarbons present were determined using a 25-foot length of 1/4-inch tubing packed with β,β' -oxydipropionitrile on Chromosorb, while operating at 100° C. and a helium flow rate of 55 ml. per minute.

AQUEOUS LAYER PRODUCTS. Formaldehyde was determined by the chromotropic acid procedure (1). The other oxygenated compounds were isolated by carefully fractionating a portion of the aqueous layer, to concentrate the organic material boiling below 100° C. The distillate was then analyzed by gas chromatography using the β,β' -oxydipropionitrile column. In some cases the individual fractions were analyzed separately. Finally, a portion of the aqueous layer was distilled to dryness under reduced pressure to isolate any residual products (glycols, aldehyde polymers) present.

Analyses of the gaseous products and of hydrocarbon mixtures by gas chromatography were corrected using the average relative response values of Rosie and Grob (3). No corrections were applied to the analyses of mixtures of oxygenated compounds, since the relative response values were not available; instead, peak areas were assumed to represent percentage by weight. Thus, the compositions of oxygenated compounds are subject to some error.

To characterize certain oxygenated compounds in the products it was necessary to synthesize samples of all possible C₄ epoxides.

Threshold Temperatures and Ease of Oxidation. The threshold temperatures required for the oxidation of various hydrocarbons varied considerably with hydrocarbon structure. This effect is best shown by the data of Table I, in which the relative reactivities of the light hydrocarbons are compared with those of *n*-hexane and "iso-octane."

Products from Oxidations of a Variety of Light Hydrocarbons. The major products resulting from the oxidations of the light hydrocarbons are summarized in Table II and Figure 1. Each experiment listed was carried out at as low a temperature as was practical for the operating conditions employed. As the data show, hydrocarbons which reacted at relatively low temperatures gave the greatest yields of oxygenated products. For hydrocarbons which required higher temperatures for oxidation, either olefins (for ethane, propane, and isobutane) or the carbon oxides (for 2-butene and isobutene) were the major products.

Epoxides were relatively minor products of these oxidations; on the other hand, for hexane and higher hydrocarbons, epoxides were major products (2). This difference is believed to be a result of the nature of the favored reaction, which appears to involve attack at an inner carbon atom, followed by formation of a five-membered ring; thus, the C₄ hydrocarbons would not be expected to give a high epoxide yield.

Further, the data of Table II indicate that whereas *n*-

Table I. Threshold Temperatures Required for Oxidizing Hydrocarbons in the Raining Solids Reactor

Solids used. 300-micron zircon silica
 Solids rate. 10 to 30 pounds per gram-mole of oxygen
 Contact time. 5 to 10 seconds
 Oxygen-hydrocarbon mole ratio in feed. 0.5

Hydrocarbon Feed	Temperature, ° C. at Which	
	Reaction essentially complete; over 85 to 90% of oxygen converted	Slow reaction began; about 10 to 20% of oxygen converted
<i>n</i> -Hexane	330	320
<i>n</i> -Butane	350	340
Isobutane	375	360
1-Butene	420	360
Iso-octane	450	380
2-Butene	515	430
Isobutene	520	460
Propane	540	470
Ethane	600	...

butane favors the production of methanol and acetaldehyde, isobutane gives acetone and isobutyraldehyde, while 1-butene gives propionaldehyde and isopropyl alcohol.

Oxidation of *n*-Butane. The maximum quantity of oxygenated compounds is obtained from *n*-butane by employing a low reaction temperature and a relatively high rate of solids flow (Table II and Figure 2). Thus, as the solids rate is increased over the range shown, the yield of oxygenated compounds also increases. The data demonstrate that the increased yield of oxygenated material is obtained at the expense of olefins. Further, as shown by Figure 3, as the solids flow rate is raised, the hydrocarbon conversion per pass decreases.

EFFECT OF CONTACT TIME. The data of Figure 4 indicate that as the contact time is doubled, the yield of the carbon oxides is increased at the expense of olefins and oxygenated products. The longer contact time also favors a greater conversion of hydrocarbon feed.

Air as Oxidant. Instead of oxygen, air may be used as the oxidant for the light hydrocarbons. In Table III comparison may be made with experiments in which oxygen was used. Although the data are not directly comparable, since the solids flow rate varied greatly for the two cases, the data indicate that the use of air may represent milder conditions and increased yields of epoxides.

Compositions of Epoxide Mixtures. The epoxide mixture obtained from *n*-butane was composed largely of 2,3-epoxybutane but contained some 1,2-epoxybutane as well as small proportions of ethylene and propylene oxides. No tetrahydrofuran was found. The epoxide mixture from isobutane consisted largely (90%) of 1,3-epoxy-2-methylpropane;

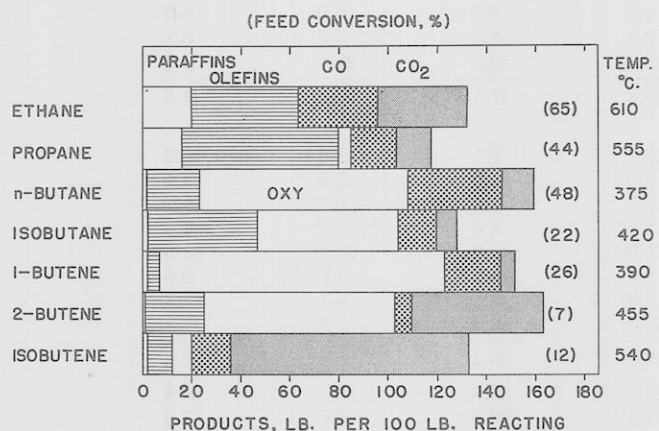


Figure 1. Products from gaseous hydrocarbon oxidations

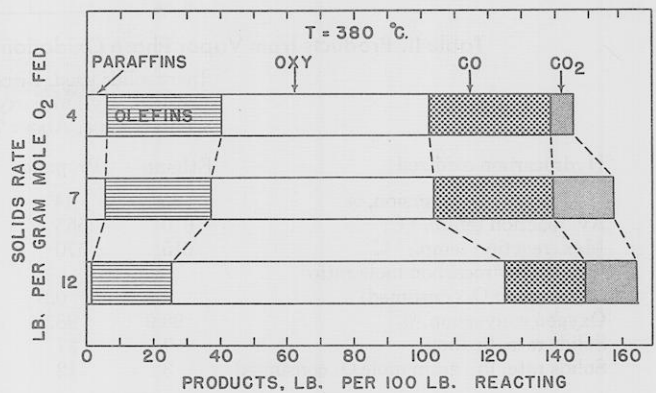


Figure 2. Effect of solids rate on *n*-butane oxidation products

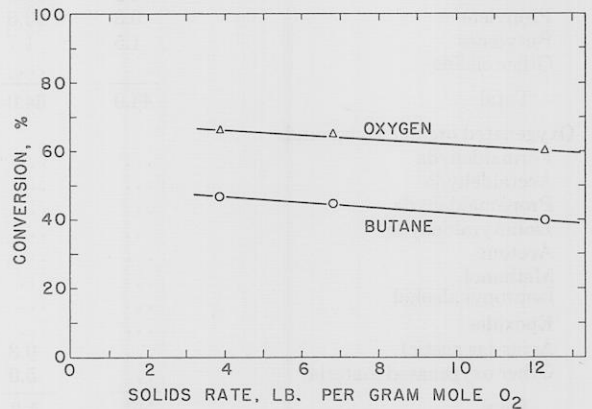


Figure 3. Effect of solid rate on feed and O₂ conversion *n*-Butane oxidation at 380° C.

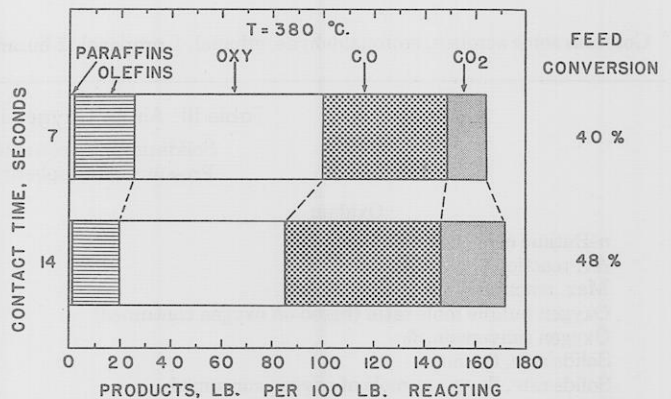


Figure 4. Effect of contact time on oxidation products *n*-Butane

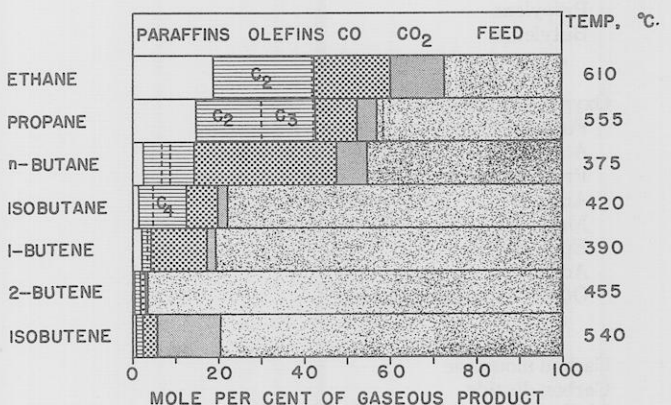


Figure 5. Exit gas from hydrocarbon oxidations

Table II. Products from Vapor Phase Oxidation of Light Hydrocarbons at Atmospheric Pressure

Inert solids used. Zircon silica, 300 microns
Oxidant. Cylinder oxygen
Contact time. About 7 seconds

Hydrocarbon oxidized	Ethane	Propane	<u>n-Butane</u>		Isobutane	1-Butene	2-Butene	Isobutene
Hydrocarbon conversion, %	65	44	25	48	22	26	16	12
Av. reaction temp., ° C.	610	555	380	375	420	390	525	540
Max. reaction temp., ° C.	615	570	390	380	430	405	525	545
Oxygen hydrocarbon mole ratio (based on O ₂ consumed)	0.9	0.5	0.5	1.1	0.35	0.37	0.33	0.30
Oxygen conversion, %	98.0	98.0	99.8	72.5	63.0	91.3	83.8	75.0
Solids rate, lb./hour	7	27	8.5	52	39	33	33	33
Solids rate, lb./gram mole O ₂ consumed	3	12	1.5	10.8	24	26	26	28
Products, Pounds per 100 Pounds of Hydrocarbon Reacted								
Olefins								
Ethylene	42.2	28.5	8.0	5.0	0.3	2.5	2.4	2
Propylene	0.3	33.8	6.1	3.2	9.7	0.8	3.6	8
Butylenes	1.5	1.7	27.4	13.1	35.1
Other olefins	1.4	1.2	...
Total	44.0	64.0	41.5	21.3	45.1	4.7	7.2	10
Oxygenated organic compounds								
Formaldehyde	12.2	10.8	5.7	12.9	7.4	8.0
Acetaldehyde	9.0	11.4	4.1	7.2
Propionaldehyde	0.7	1.7	0.7	20.5
Isobutyraldehyde	7.7
Acetone	1.9	5.7	16.2	3.2	20.4	...
Methanol	21.3	23.8	4.6	10.0
Isopropyl alcohol	9.0
Epoxides	0.6	9.8	11.7	14.5
Acids (as acetic)	...	0.3	3.3	11.4	2.8	5.8
Other oxygenated material	...	5.0	7.4	10.5	3.5	33.3 ^a	11.2	...
Total	Nil	5.3	56.4	81.1	57.0	116.4	39.0	...
Carbon monoxide	32.1	18.2	28.8	38.3	15.7	22.9	11.0	16.0
Carbon dioxide	36.3	14.2	7.0	12.9	8.3	5.6	62.8	107.0
Methane plus some higher paraffins	19.7	15.8	6.1	1.6	2.0	2.0	...	2.0

^a Contains some acrolein, crotonaldehyde, ethanol, 1-propanol, 2-butanol, 2-butanone, pentanones, 2,3-butanedione, and butanediols.

Table III. Air vs. Oxygen in Oxidation of n-Butane

Solids used. Zircon silica, 300 microns
Pressure. Atmospheric

Oxidant	Air		Oxygen	
n-Butane conversion, %	20	27	24	25
Av. reaction temp., ° C.	375	385	380	380
Max. reaction temp., ° C.	390	395	390	390
Oxygen butane mole ratio (based on oxygen consumed)	0.28	0.33	0.50	0.50
Oxygen conversion, %	57	79	99	100
Solids rate, lb./hour	33	25	20	9
Solids rate, lb./gram-mole of oxygen consumed	41	23	4	2
Contact time, seconds	5	5	8	8
Products, Pounds per 100 Pounds of Butane Reacting				
Olefins				
Ethylene	4.1	5.0	6.0	8.0
Propylene	2.4	3.8	4.5	6.1
Butylenes	28.8	32.3	27.4	27.4
Total	35.3	41.1	37.9	41.5
Oxygenated organic compounds				
Formaldehyde	10.2	9.1	11.6	12.2
Acetaldehyde	4.0	11.0	8.9	9.0
Propionaldehyde	0.7	1.0	0.7	0.7
Acetone	5.5	4.4	1.7	1.9
Methanol	18.3	15.2	22.2	21.3
Epoxides	9.4	6.3	1.8	0.6
Acids	5.9	5.3	4.1	3.3
Other oxygenated material	12.3	12.9	7.4	7.4
Total	66.3	65.2	58.4	56.4
Carbon monoxide	20.2	23.7	33.4	28.8
Carbon dioxide	11.8	10.0	8.6	7.0
Methane plus some other paraffins	3.6	1.8	4.7	6.1

some 1,2-epoxy-2-methylpropane (8%) was also present. For the case of 1-butene the epoxide mixture consisted largely of 1,3- and 2,3-epoxybutanes as well as some ethylene and propylene oxides. No 1,2-epoxybutane was found.

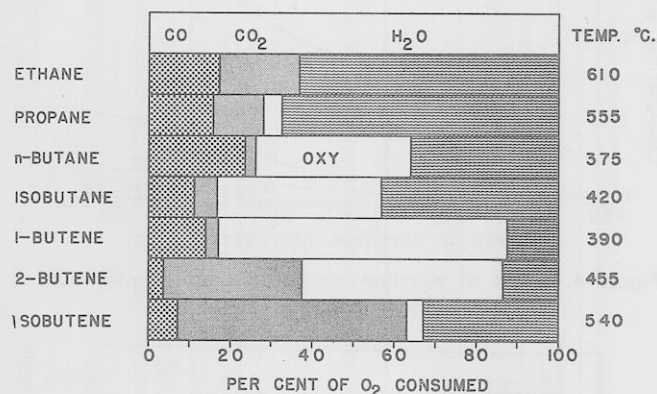


Figure 6. Oxygen distribution during oxidation of hydrocarbons

Exit Gas Composition. Figure 5 illustrates the compositions of the exit gas obtained. In many cases these gases could be recycled to the reaction zone.

Oxygen Distribution. The proportions of oxygen appearing in the various reaction products as carbon oxides, water, and organic oxygenated compounds are shown in Figure 6.

ACKNOWLEDGMENT

The authors are indebted to Robert V. Digman and Roy A. Jordan of this laboratory, who synthesized the epoxides needed for the characterization work, and to Esso Research and Engineering Co. for financial support and technical assistance.

LITERATURE CITED

- (1) Bricker, C.E., Johnson, H.R., *Anal. Chem.* 17, 400 (1945).
- (2) Jones, J.H., Fenske, M.R., *Ind. Eng. Chem.* 51, 262 (1959).
- (3) Rosie, D.M., Grob, R.L., *Anal. Chem.* 29, 1263 (1957).

RECEIVED for review July 29, 1960. Accepted January 9, 1961. Symposium on Combustion, Division of Petroleum Chemistry, 136th Meeting, ACS, Atlantic City, N. J., September 1959.

Vapor Phase Oxidation of Aromatic Hydrocarbons

JENNINGS H. JONES, MERRELL R. FENSKE, DAVID G. HUTTON, and H. DONALD ALLENDORF
Petroleum Refining Laboratory, The Pennsylvania State University, University Park, Pa.

A "RAIN" of fine solids which remove reaction heat and prevent combustion in vapor phase oxidation reactions has been further studied. The solids needed for good temperature control occupy only a small proportion of the reaction zone and thus allow reaction in essentially an open tube.

The utility of the present reactor in the oxidation of paraffin hydrocarbons ranging from ethane to a paraffin wax as well as of certain olefin hydrocarbons has been described (2, 3). This article presents the results obtained for a variety of aromatic hydrocarbons.

APPARATUS

The apparatus has been described (3). The solids circulated for heat removal consisted of fused zircon silica (The Carborundum Co.) about 300 microns in diameter. Cylinder oxygen (purity 98.5%) was the oxidant, equally distributed through four separate inlets along the length of the reaction zone.

EXPERIMENTAL RESULTS

No attempt was made to determine the optimum reaction conditions for any single product or type of products; all experiments reported are of an exploratory nature.

The quantities of hydrocarbons subjected to oxidation varied from about 300 to 2000 grams. Material balances for the experiments varied from 90 to 100%; however, to express the results on a common basis, all data were calculated using carbon and oxygen balances based on the quantities of products actually found.

Source of Materials. The hydrocarbons used as feeds were purified by careful fractionation and possessed the following properties (boiling point, ° C., refractive index, n_D^{20} , and estimated purity, %, listed in order in parentheses following the name of each hydrocarbon): toluene (110.7° C. at 760 mm., 1.4969, 99+ %); ethylbenzene (131.15° C. at 760 mm.,

1.4959, 99+ %); isopropylbenzene (152.4° C. at 760 mm., 1.4910, 99+ %); 1,2,4-trimethylbenzene (169.4° C. at 760 mm., 1.5047, 98+ %), and a mixture of 1,2- and 1,3-diisopropylbenzenes (203.4° C. at 760 mm., 1.4908, 95+ %).

Product Analyses. The oxidation products consisted of noncondensable gas, an organic layer rich in hydrocarbons and oxygenated compounds, and an aqueous layer consisting largely of water from the steam used to lift the cycling solids but also containing the water of reaction and some water-soluble oxygenated compounds. Vapor-liquid gas chromatographic procedures were used extensively in the analytical work but, in addition, all of the major reaction products were isolated in quantity by distillation techniques, and compound identifications were made using standard qualitative and quantitative analytical procedures.

A Perkin-Elmer Model 154 C unit was used for the gas chromatographic analyses. The gaseous products were analyzed for C₂ to C₆ hydrocarbons and carbon dioxide using a 25-foot column packed with hexamethylphosphoramide on Chromosorb at 30° C. Hydrogen, oxygen, nitrogen, methane, and carbon monoxide were separated on a 20-foot column packed with Linde 5A Molecular Sieves at 100° C. Analyses of the gaseous products were corrected using average relative thermal response values.

The organic layer products from the experiments on toluene, ethylbenzene, and isopropylbenzene were analyzed using a 20-foot column packed with Carbowax 1500 on Chromosorb, operated at 100° C. and a helium flow rate of 68 ml. per minute. All of the compounds present were eluted in this column, but some of the lower boiling products were not separated. For this reason, the organic layer product was also analyzed using a 25-foot column packed with β,β' -oxydipropionitrile operated at 100° C. and a helium flow rate of 57 ml. per minute. The final analysis was determined by combining the results obtained from these two columns.