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.

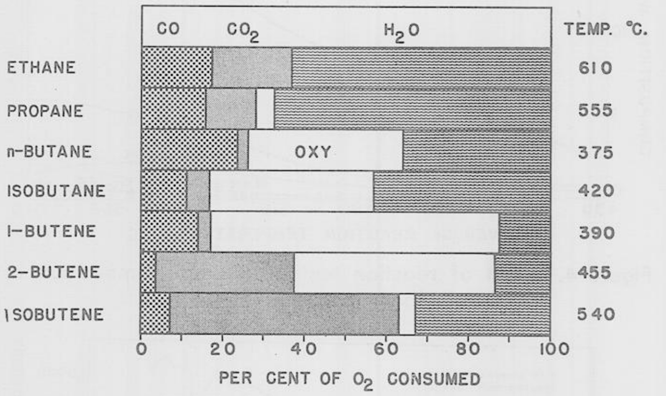

Figure 6. Oxygen distribution during oxidation of hydrocarbons

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.

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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).

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Vapor Phase Oxidation of Aromatic Hydrocarbons

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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, $n^{20}D$, 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 C_2 to C_6 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.

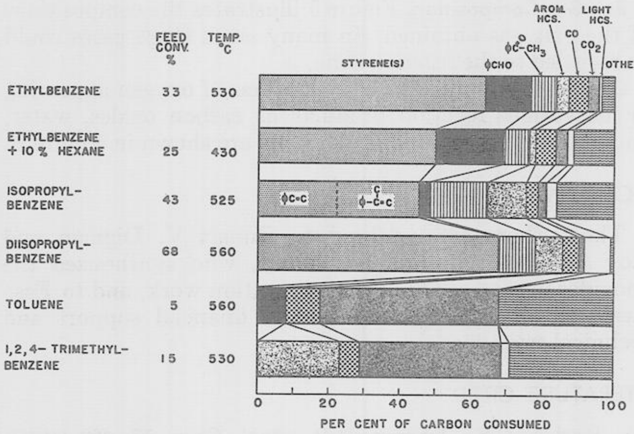

Figure 1. Yield of products from aromatics

Carbon balance

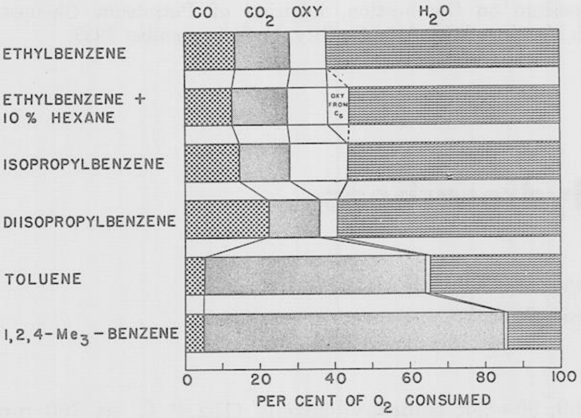

Figure 2. Oxygen distribution for oxidation of aromatics

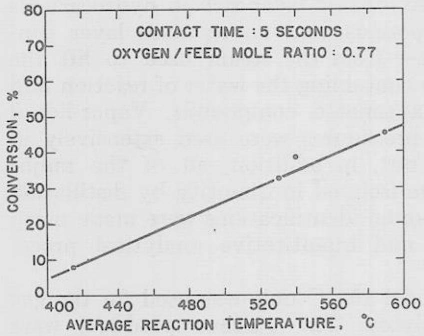

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Figure 3. Effect of temperature on feed conversion

Ethylbenzene oxidation

Samples of the various organic layers also were analyzed using careful fractional distillations, by means of which many products were isolated and identified by preparing known derivatives; functional groups were determined quantitatively by standard analytical methods.

A major portion of each water layer was distilled through an efficient glass helices–packed distillation column to recover the organic material distilling below 100° C. This material was analyzed by vapor phase gas chromatography using Carbowax 1500 and β,β'-oxydipropionitrile columns. Average relative response values were not used in this analysis, since they were not available for all the compounds present in either the organic layer or the water layer organic material. No appreciable amount of residual organic material was isolated from the aqueous layer on stripping off the water to dryness under vacuum.

Formaldehyde in the water layers was determined by the chromotropic acid procedure (*1*), and acids (assumed to be acetic acid) were titrated with standard base.

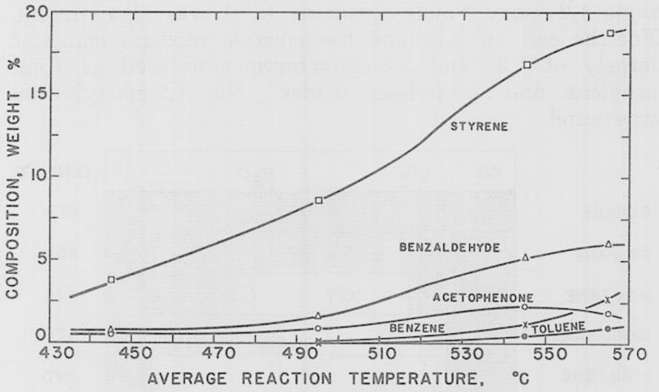

Figure 4. Effect of reaction temperature on composition of ethylbenzene organic layer

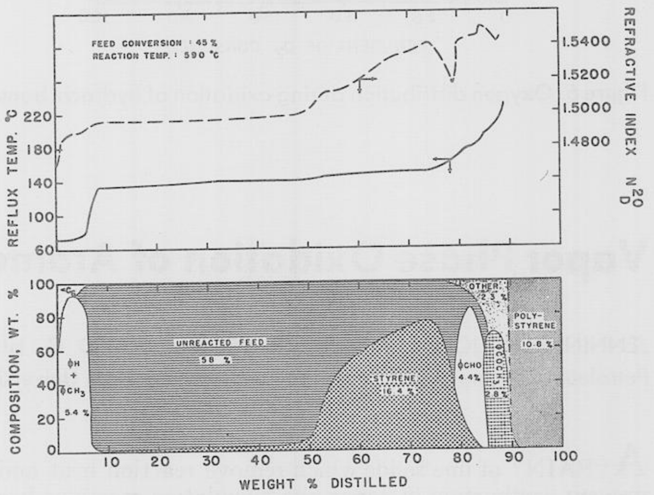

Figure 5. Distillation of ethylbenzene products

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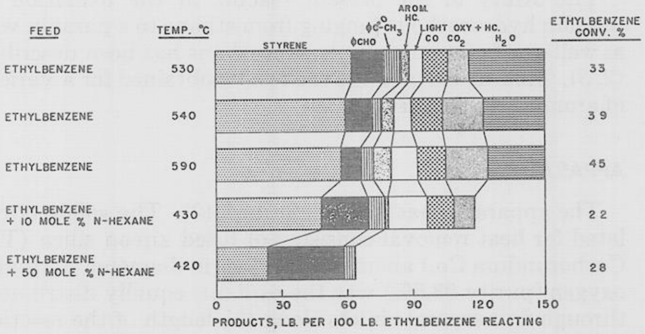

Figure 6. Products from ethylbenzene oxidations

Ease of Oxidation. In contrast to the behavior of paraffin and cycloparaffin hydrocarbons of similar carbon content, aromatic hydrocarbons are difficult to oxidize at atmospheric pressure and require elevated temperatures. Aromatic hydrocarbons containing side chains of only a single carbon atom (toluene and 1,2,4-trimethylbenzene are examples) require a temperature of at least 500° to 550° C. before any appreciable reaction occurs and yield carbon dioxide and water as the major products. Aromatic hydrocarbons containing side chains at least two carbon atoms long (ethylbenzene and isopropylbenzene are examples) slowly react at temperatures ranging from 450° to 500° C. to give styrene, styrene derivatives, and oxygenated compounds such as acetophenone and benzaldehyde as major products.

The variety and yields of products obtained from the various aromatics are tabulated in Figure 1, while Figure 2 shows the distribution of oxygen. The operating conditions for the experiments appear in Table I.

Table I. Operating Data for Vapor Phase Oxidations of Aromatic Hydrocarbons at Atmospheric Pressure

Inert solids circulated. Zircon silica, 300 microns Oxidant. Cylinder oxygen, 98.5%

Feed	Toluene	Ethylbenzene				Isopropylbenzene		Me$_3$-benzene[a]	Diisopr-benzene[b]	nC$_6$(10%), C$_6$H$_5$Et 90%[c]	nC$_6$(50%), C$_6$H$_5$Et 50%[d]
Experiment No.	1	2	3	4	5	6	7	8	9	10	11
Feed conversion, %	4.6	38.5	32.6	45	8	43	58	17.5	61.5	24.5	40.4
Oxygen conversion, %	37.5	79.4	72.1	97.5	28.0	81.9	96.0	91.6	98	50.9	98.5
Oxygen feed mole ratio (based on O$_2$ charged)	0.72	0.77	0.70	0.70	0.71	0.75	0.74	1.03	0.77	0.69	0.69
Lb. O$_2$/100 lb. of hydrocarbon feed (based on O$_2$ consumed)	9.2	23.1	15.3	20.4	6.1	16.4	18.8	25.0	15.0	10.8	22.5
Contact time, seconds	5	5	5	4	5	5	5	9	7	5	5
Solids rate, lb./g.-mole O$_2$ reacting	21.6	14.5	16.0	10.0	10.5	14.3	10	16	15	20.7	10
Average reaction temp., ° C.	560	540	530	590	415	525	560	532	560	430	423
Charge data											
Feed charged, grams	325	785	853	1949	832	906	515	639	735	846	1236
Oxygen charged, grams	77	181	181	408	182	181	101	175	113	179	282
Water as solids lift, grams	781	1799	1788	2632	1405	1837	760	2016	1365	1867	2148
Duration of experiment, minutes	51	120	120	250	120	120	70	180	107	120	180
Product data											
Organic layer, grams	293	683	790	1775	798	813	447	562	560	778	1008
Water layer (total), grams	816	1890	1897	2712	1405	1935	780	2035	1474	1932	2420
C.H.O. in noncond. gas, grams	74	142	113	435	168	109	96	157	112	129	161
Vol. of dry gas at s.t.p., cu. ft.	1.9	4.1	3.6	12.5	4.4	3.1	2.5	3.7	3.8	4.1	5.1

[a] 1,2,4-Trimethylbenzene. [b] 1,2- and 1,3-diisopropylbenzene. [c] Hexane, 10 mole %; ethylbenzene, 90 mole %. [d] Hexane, 50 mole %; ethylbenzene, 50 mole %.

Toluene, Trimethylbenzene, and Benzene. Under the conditions studied, the threshold temperature for the oxidation of toluene was about 550° C. Below this temperature little or no oxygen reacted. Even at 560° C. an oxygen conversion of only 37.5% was observed when an oxygen-feed mole ratio of 0.72 was used. The major products from the oxidation of toluene were the carbon oxides and water. Benzaldehyde was produced to the extent of about 8.6 pounds per 100 pounds of toluene reacting. Small quantities of light oxygenated compounds also resulted but were not identified, since the low feed conversion (4.6%) was not favorable for an accurate evaluation of these products.

Trimethylbenzene behaved much like toluene, giving carbon dioxide and water as the major products. Benzene was even less reactive than toluene and behaved similarly.

The ratios of carbon dioxide to water appearing in the products from benzene, toluene, and trimethylbenzene were characteristic of combustion reactions.

Ethylbenzene. This hydrocarbon required a temperature of about 500° C. before any appreciable reaction occurred at the conditions studied. At lower temperatures the reaction was much slower, as shown by Figure 3.

The major products of the reaction were styrene, benzaldehyde, and acetophenone; benzene and toluene were formed in minor proportions. The effect of temperature on the yield of products resulting from ethylbenzene is shown by Figure 4, which indicates that benzene and toluene begin to form at about 500° C.

The composition of a typical liquid organic layer product obtained from ethylbenzene is illustrated in Figure 5, in which the products present were isolated by distillation under reduced pressure (30 mm. of mercury) in a column having about 15 theoretical plates and operating at a reflux ratio of at least 10 to 1. In addition to using gas chromatographic procedures for analysis, the major products also were identified as follows: Styrene was converted to its dibromo derivative, melting point 72.5–3° C. A mixed melting point with an authentic sample of dibromostyrene (melting point 72.8°–3.8° C.) showed no depression. Benzaldehyde was identified by preparation of its *p*-nitrophenylhydrazone melting at 188.4° to 192.4° C. A mixed melting point with an authentic sample of the derivative (melting point 192°–3.7° C.) showed no depression. Acetophenone was identified by conversion to its *p*-nitrophenylhydrazone which melted at 183.4–5.4° C. A mixed melting point with an authentic sample of the derivative (melting point 183.9° to 185.9° C.) showed no depression.

In experiments made at relatively high temperature levels (2 and 4, Table I), a small proportion of carbon was produced and appeared in the products as a smoke. This carbon formation was accompanied by a higher production of carbon dioxide (see Figure 6). On lowering the reaction temperature to about 530° C. (experiment 3, Table I), the carbon formation was eliminated and the yield of carbon dioxide dropped.

Ethylbenzene-Hexane Mixtures. Mixtures of these two hydrocarbons containing 90 and 50 mole %, respectively, of the aromatic hydrocarbon were oxidized at relatively low temperatures to determine if the paraffin would initiate reaction of the aromatic at a lower temperature. As the data of Figure 6 (see also Figure 1) show, while hexane tended to initiate reaction at a lower temperature, it had no appreciable effect on the yield of products (other than to increase the yield of benzaldehyde slightly). Thus, in experiment 5 (Table I) in which pure ethylbenzene was used as the feed, only 28% of the oxygen reacted and the average reaction temperature was 415° C. On the other hand, in experiment 10, in which the feed contained 10 mole % of *n*-hexane, 51% of the oxygen reacted and the average reaction temperature rose to 430° C., although all other conditions were identical in both experiments.

In the latter experiment in which the feed contained

10 mole % of hexane, about 50% of the hexane and 22% of the ethylbenzene were converted.

In experiment 11 the hexane content of the feed was increased to 50 mole %. This experiment was made at a low temperature level, under which conditions 28% of the ethylbenzene and 56% of the hexane were converted. On the basis of the ethylbenzene reacting, the yield of benzaldehyde was increased considerably, as shown in Figure 6.

Isopropylbenzene. This compound readily oxidized at temperatures above 500° C. at atmospheric pressure. The major products of the reaction consisted of styrene, α-methylstyrene, acetophenone, and benzaldehyde. The relative proportions produced are given in Figure 1. The composition of a typical organic layer product as determined by distillation is presented in Figure 7. The distillation was carried out under reduced pressure (20 mm. of mercury) using a glass-packed column having about six theoretical plates, and operated at a reflux ratio of about 5 or 10 to 1.

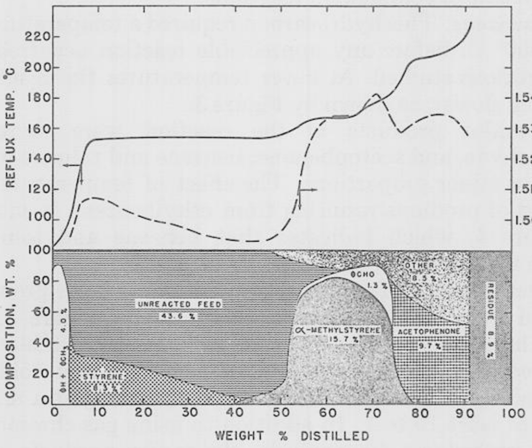

Figure 7. Distillation of isopropylbenzene products

The reaction products were identified by gas chromatographic procedures as well as by the preparation of known derivatives as outlined under ethylbenzene.

Diisopropylbenzene. This compound readily oxidized to give styrene and oxygenated derivatives as principal products. Although none of the individual compounds were identified, the presence of isopropylstyrene, isopropyl-α-methylstyrene, and carbonylic compounds was indicated on carefully distilling portions of the liquid product. The relative proportion of each product in the distillate was estimated on the basis of the unsaturation and carbonyl content of the various boiling ranges. The data are summarized in Figure 1.

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LITERATURE CITED

(1) Bricker, C.E., Johnson, H.R., *Anal. Chem.* 17, 400 (1945).
(2) Jones, J.H., Allendorf, H.D., Hutton, D.G., Fenske, M.R., J. Chem. Eng. Data. 6, 620 (1961).
(3) Jones, J.H., Fenske, M.R., *Ind. Eng. Chem.* 51, 262 (1959).

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Flame Luminosities of Hydrocarbons and Hydrocarbon Mixtures Burned in the Gas Phase

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DURING THE COMBUSTION of a hydrocarbon fuel in a jet engine, the extent to which microscopic carbonaceous particles form in the flame can substantially affect engine performance (*6*). Incandescent carbonaceous particles increase the rate of radiant energy transmission to the walls of the combustion chamber, resulting in increased wall temperatures. Excessive wall temperature shortens combustion chamber life, and incomplete combustion of the fuel represents a loss in fuel efficiency, leading to decreased range and payload. Therefore advantages could accrue from use of a jet fuel with little tendency to form carbon in the flame. Although carbon formation can also be controlled by modifications of engine design such as premixing techniques or varying fuel-air ratio, accompanying space, weight, or other penalties may make it impractical.

This investigation was undertaken in connection with a project to study the feasibility of cooling very high speed aircraft by means of an endothermic reaction of the fuel prior to combustion. A number of endothermic reactions of hydrocarbons have been under consideration for this purpose, including aromatization, cracking, depolymerization, dehydrogenation, and isomerization. In evaluating each reaction one of the criteria has been the burning characteristics of the products, particularly the luminosity.

The carbon-forming propensities of fuels have usually been measured and compared by determining the maximum rate at which each fuel could be burned in a specially designed apparatus (*3, 4, 5*) without smoking. The figure of merit may be the actual limiting burning rate or the corresponding flame height. In some cases smoking charac-