180. *The Oxidation of Ethylene and Propylene in the Gas Phase.*

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The products of reaction of ethylene and propylene with air have been studied in a flow system, particular attention being given to propylene. The oxidation of propylene in a Pyrex tube at and above atmospheric pressure shows the " negative temperature coefficient " previously observed with the paraffins, and the survival of intermediate products has been examined in relation to this effect. In a mild steel tube intermediates fail to survive and the system of reaction at low temperature disappears. With increasing pressure, however, these features are progressively restored.

The results extend those of Lenher and of Newitt and Mene under other conditions of temperature and pressure but are consistent with them. The present work shows that most of the ethylene or propylene which reacts generally appears in the products as higher olefins.

STUDIES of the gas-phase oxidation of olefins have been concerned primarily with ethylene. Newitt and Mene (*J.*, 1946, 97) examined the products of oxidation of propylene at high pressure, and Lenher (*J. Amer. Chem. Soc.*, 1932, **54**, 1830) reported some experiments on its oxidation in a flow system at normal pressure. The main purpose of the work now to be described was to study the products formed from propylene under conditions intermediate between those employed in the two earlier investigations, and thus to complete a general picture of the products obtainable from propylene by homogeneous reaction with oxygen. Preliminary results with ethylene are also reported for comparison with those of Lenher (*J. Amer. Chem. Soc.*, 1931, **53**, 3737, 3752) which were obtained under somewhat similar conditions.

EXPERIMENTAL

Materials.—The ethylene used in these experiments was supplied by the British Oxygen Company, in cylinders. An analysis by standard techniques showed 99·5% of olefin, the remainder being mainly nitrogen. The gas was used without further treatment, except that in some experiments it was passed over zinc chloride to remove traces of aldehyde.

Propylene was obtained by dehydration of *iso*propanol from American sources. Its vapour density indicated a molecular weight corresponding to pure propylene, and exhaustive fractionation failed to reveal any higher hydrocarbons. The gas was completely absorbed by standard olefin reagents. It was used without further purification.

Other reagents used were of standard analytical quality.

Apparatus and Method.—The apparatus was similar to that used by Burgoyne and Silk (*J.*, 1951, 572) for the flow-oxidation of methyl*cyclo*pentane. In addition to the Pyrex glass reactor, however, a mild-steel reactor of similar size, with a stainless-steel preheater tube, was also used. With both reactors certain experiments were carried out at elevated pressures and these necessitated special arrangements for the control of flow.

In order to facilitate both the preliminary exploration for suitable reaction conditions and the control of runs for analytical purposes, an oxygen indicator was constructed, by means of which it was possible to observe directly the oxygen content of the outlet gases. The instrument employed the polarographic method and was similar to that described by Wise (*Chem. and Ind.*, 1948, 37) but with the modified absorption cell illustrated in Fig. 1. Except when a reading was being taken, the gaseous products bubbled through the solution of potassium chloride containing methyl-red *via* the sintered-glass disc. When a reading was being taken the gas was allowed to by-pass the bubbler.

Methods of Analysis.—Vacuum distillation. For the qualitative analysis of some of the reaction products a modified vacuum-distillation apparatus based on Stock's design was used. By this means materials boiling in the range −100° to +80° could be separated and the vapour pressure and molecular weight of the separated fractions determined directly.

Quantitative analysis. The condensed products were dissolved and diluted to standard volume in alcohol which had been refluxed for 6 hours over sodium hydroxide and then distilled through a 20-in. column. The solvent was neutral to indicators and gave no aldehyde colour with Schiff's reagent. Portions of the solution were taken for the following determinations.

Total acids. The solution was titrated with 0·1N-sodium hydroxide (phenolphthalein or thymolphthalein).

Formic acid. The solution was made slightly alkaline with sodium hydroxide, evaporated to dryness and heated at 110° for 1 hour to remove volatile matter. Excess of 10% sulphuric acid was added and organic acids were distilled off. The distillate was diluted to standard volume, and to aliquot portions excess of sodium carbonate solution was added. The formate was treated with a slight excess of 0·1N-potassium permanganate. A measured excess of 0·1N-sodium oxalate was added, and the solution acidified with sulphuric acid and warmed to 60°. The remaining oxalate was titrated with permanganate. The equivalent of the formate was found by subtracting that of the oxalate from the total permanganate titre.

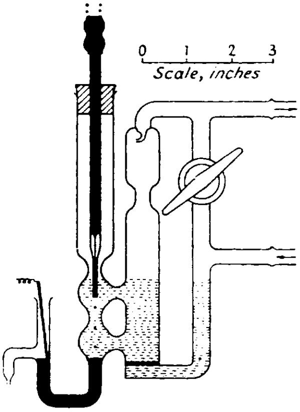


FIG. 1. *Polarograph absorption cell.*

Total aldehyde. Ripper's method (*Monatsh.*, 1900, **21**, 1079) was chiefly used.

Formaldehyde. This was determined colorimetrically with Schiff's reagent and 10% of sulphuric acid. The results were high if formaldehyde amounted to less than 30% of the total aldehyde, but otherwise satisfactory.

Acetaldehyde. To a portion of the solution containing about 0·1 mg. of acetaldehyde, 1 ml. of 10% alcoholic piperidine was added and the mixture diluted to 50 ml. Solutions for comparison were made up similarly from 1% or 0·1% acetaldehyde solution. To sample and standards were added simultaneously 5 ml. of freshly-prepared 1% sodium nitroprusside solution and after 1 min. colours were compared. The blue-green colour was fugitive. Formaldehyde did not interfere but propaldehyde caused results to be high to the extent of about 5% of the propaldehyde present.

Peroxide. Excess of 20% potassium iodide was added to the solution contained in a stoppered flask. The air in the flask was displaced with carbon dioxide and 10% sulphuric acid run in, together with a few drops of ferrous sulphate solution. After 1 hour the liberated iodine was titrated with standard thiosulphate.

Olefinic bonds. A measured excess of 0·1N-potassium bromate containing excess of bromide was added to the solution, which was then cooled to 0° and treated with 10 ml. of 10% sulphuric acid. After 30 min. at 0° excess of potassium iodide was added and the liberated iodine titrated with thiosulphate.

The difference between the titre and that of a blank carried out simultaneously was equivalent to the olefinic bonds in the initial solution.

Gases. The gas sample was analysed in a Bone–Newitt apparatus, potassium hydroxide being used for carbon dioxide, alkaline pyrogallol for oxygen, mercuric perchlorate for olefins, and ammoniacal cuprous chloride for carbon monoxide. Hydrogen and saturated hydrocarbons were estimated by explosion of the residue with excess of oxygen.

The reagent for olefins was prepared by mixing 150 g. (95 ml.) of 60% perchloric acid with 45 g. of mercuric oxide and adjustment to 300 ml. with water. The reagent was kept for 24 hours and filtered if necessary. It was rapid and clean in use, giving full absorption up to 100% olefin in one operation. No precipitate was formed, since mercurous perchlorate is soluble in water.

RESULTS

Oxidation of Ethylene.—The experiments with ethylene were all done in the Pyrex glass reactor. First, the relation between temperature and mean time of residence necessary for reaction to begin in a 2 : 1 ethylene–air mixture was determined, with the results shown in Fig. 2. The onset of reaction was detected by the first appearance of aldehyde in the outlet gases, as indicated by periodic Schiff's tests. Even at long residence times the reaction does not begin much below 290°.

Preliminary runs with the 2 : 1 ethylene–air mixture at 500° yielded (*a*) a pale yellow aqueous condensate in the 0° trap, and (*b*) a mixture of colourless aqueous condensate with a yellow non-aqueous material in the −78° trap. The aqueous fractions contained acids (formic and acetic), aldehydes (formaldehyde and a little acetaldehyde), peroxide, alcohol, and traces of ethylene glycol and ethylene oxide. The non-aqueous condensate appears to correspond to material obtained under similar conditions by Lenher (*loc. cit.*, 1931). The initial b. p. was 20° and the fractions separated by distillation through a 20-in. column are shown in Table 1, together with the results of determinations of molecular weight, total aldehyde, and olefinic bonds in certain cases. Owing to inadequate condensation there were considerable losses of material from the lower fractions, which were white, intensely lachrymatory liquids. The fractions boiling above 80° were increasingly yellow, and the fraction above 110° condensed to a white odourless solid.

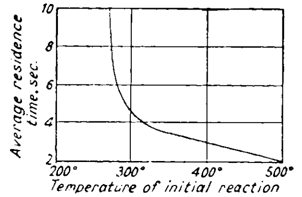


FIG. 2. *Variation with temperature of average residence time for onset of reaction of 2 : 1 ethylene–air mixture.*

TABLE 1. *Products of fractional distillation of* 50 *ml. of non-aqueous condensate formed by reaction of* 2 : 1 *ethylene–air mixture at* 500° C (*mean residence time,* 6 *sec.*)

Fraction no.	Boiling range, ° C	Volume, ml.	Mol. wt.	Aldehyde, %	Olefin, %
1	20—30	2·1	—	—	—
2	30—40	1·5	72	—	—
3	40—50	2·4	68	30	60
4	50—60	2·2	71	—	—
5	60—68	2·9	73	—	—
6	68—73	1·5	88	22	30
7	73—80	1·2	92	—	—
8	80—100	2·2	—	—	—
9	100—110	1·5	—	—	—
10	110—120	0·6	—	—	—
11	120—130	0·3	—	—	—

The observed properties of the fractions suggest that they consisted of saturated and unsaturated hydrocarbons and aldehydes. The smell and lachrymatory characteristics may be attributed to the unsaturated aldehydes. The solid fraction showed few positive reactions and it was concluded to be the cyclic polymer of formaldehyde, trioxan (b. p. 110°).

In further runs under similar conditions the products were analysed as fully as possible and carbon balances drawn up. Some 60% of the carbon which had apparently reacted was unaccounted for in the products. This discrepancy could most easily be explained on the assumption that some of the olefinic gas in the products measured by absorption and counted as ethylene, was in fact propylene which had passed the −78° trap. This deduction was verified by explosion analysis of a known volume of the olefin constituents. In Table 2 the complete analysis of the reaction products is shown, and it will be seen that the carbon balance is reasonably good considering the complexity of the mixture.

TABLE 2. *Products of the complete reaction of a* 2 : 1 *ethylene–air mixture at* 515° C.

Mean residence time, 3 sec.; ethylene passed in, 394 g.; ethylene in outlet gases, 330 g.; ethylene reacted, 64 g.

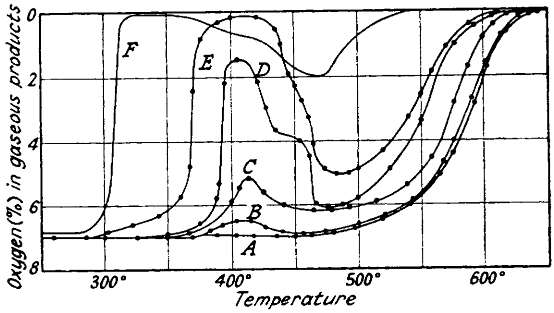
Products estimated, expressed as equivalent percentage of reacted ethylene :—

Carbon monoxide	17	higher aldehydes	1·3	C_4 olefins	8
carbon dioxide	1·0	formic acid	0·2	C_5 and higher hydrocarbons	2
formaldehyde	3·5	propylene	71	Total	104·0

Oxidation of Propylene in Pyrex Glass.—Preliminary efforts to survey the conditions for the onset of the reaction between propylene and air by the use of the aldehyde detection method were unsuccessful because propylene itself, when in saturated aqueous solution gave a faint colour with Schiff's reagent, even after being washed with sodium hydrogen sulphite solution. In consequence, the polarographic oxygen indicator was developed so as to give rapid readings of the oxygen content of the gaseous products and thus indicate the extent of reaction at any moment.

FIG. 3. *Variation in extent of reaction with rising temperature for various flow rates with* 2 : 1 *propylene–air mixture.*

A, 50 *sec.*; *B*, 70 *sec.*; *C*, 83 *sec.*; *D*, 100 *sec.*; *E*, 130 *sec., all at* 760 *mm.*; *F*, 100 *sec.*, 1160 *mm.*



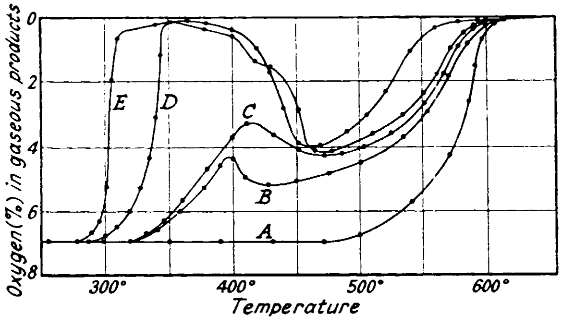


FIG. 4. *Variation in extent of reaction with falling temperature for various flow rates with* 2 : 1 *propylene–air mixture.*

A, 50 *sec.*; *B*, 70 *sec.*; *C*, 83 *sec.*; *D*, 100 *sec.*; *E*, 130 *sec.*

A propylene–air stream of fixed composition was passed through the reaction system at a constant rate of mass flow. The temperature of the system—initially cold—was slowly raised and, at intervals, corresponding readings of temperature and oxygen percentage in the outlet gas were noted. The observations were made up to 600°, whereafter the system was allowed to cool slowly and readings were continued until reaction ceased entirely.

By this means the curves shown in Figs. 3—5 were derived. The reproducibility of the results was surprisingly good. Those in Fig. 3 refer to a 2 : 1 propylene–air mixture and show the variation in extent of a reaction as the temperature is raised for different rates of flow. Fig. 4 shows behaviour under the same conditions as the temperature is lowered. Fig. 5 shows the effect of increasing temperature on the extent of reaction for different propylene : air ratios when the flow rate is constant.

The most noteworthy features of Figs. 3—5 are as follows : (1) The negative temperature coefficient of reaction velocity in the range 400—500°. (2) The " step " in certain curves at about 450°. (3) The " hysteresis " effect in the relation of rate to falling temperature. This is only partly explicable in terms of thermal lag in the reaction system and lag in operation of the polarograph; and it appears that there is a true lag in the effect of falling temperature on reaction velocity which may be associated with the part played by the surface in initiating re-reaction. (4) The long reaction periods at about 500°, compared with those for ethylene. At lower temperatures reaction periods for propylene are also long, but ethylene does not react in this range.

The products of reaction of a 2 : 1 propylene–air mixture with 100-sec. residence time (see Fig. 3) at 400° (peak of low-temperature reaction), 450° (" step " in decay of low-temperature reaction), 485° (minimum reaction rate), and 590° (typical high-temperature reaction) were then examined. Products of the reaction of the same mixture at 402° with 130-sec. residence (maximum low-temperature reaction) were also examined in a very long run which gave sufficient product for more detailed analysis. The results obtained from all these representative reactions are summarised in Table 3.

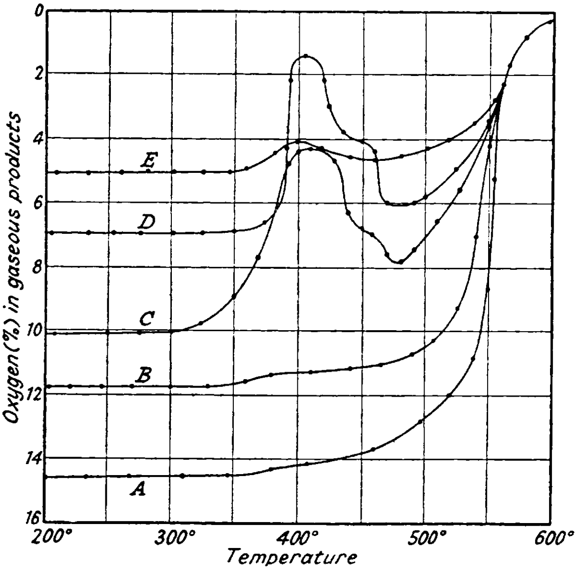


FIG. 5. *Variation in extent of reaction with rising temperature for various propylene–air mixtures at a constant flow rate (residence time of* 100 *sec.* at 20°).

A, C_3H_6 28%, O_2 15%; *B*, C_3H_6 42%, O_2 11·8%; *C*, C_3H_6 50%, O_2 10%; *D*, C_3H_6 67%, O_2 6·7%; *E*, C_3H_6 75%, O_2 5%.

TABLE 3. *Products of reaction of a* 2 : 1 *propylene–air mixture (in Pyrex glass).*

Contact time, sec. at 20° c	100	100	100	100	130
Temp., ° c	400	450	485	590	402
% carbon as :					
unchanged C_3H_6	90	89	88	87	84
CO	1·6	0·9	0·2	1·0	1·3
CO_2	0·5	0·5	0·4	0·6	0·4
HCHO	1·4	0·9	0·6	0·9	1·3
$CH_3{\cdot}CHO$	—	—	—	—	0·85
acid (as HCO_2H)	trace	trace	trace	0·05	—
C_4 hydrocarbons	4·5	4·2	1·5	5·0	1·3
C_5 hydrocarbons					0·6
peroxide	trace	trace	nil	nil	trace
deficiency	2·0	4·0	8·2	6·0	10·4
% oxygen as :					
unchanged O_2	28	42	52	3·4	7·1
CO	23	13	4	18	18·5
CO_2	13	13	14	19	8·5
HCHO	9·6	5·6	5·0	9·2	20
CH_3CHO	—	—	—	—	5·8
peroxide	trace	trace	nil	nil	trace
acid	trace	trace	trace	0·5	—
deficiency, incl. H_2O	26	26	25	51	40

To complete the work in the Pyrex glass reactor experiments were made with a 2 : 1 propylene–air mixture reacting at increased pressures and a residence time of 100 sec. (measured at 20°). The reaction–temperature curve (with ascending temperature) obtained at 1160 mm. by the use of the polarograph is included in Fig. 3. It shows the usual low- and high-temperature reaction zones but at lowered temperatures. The initial reaction commences at about 280°.

Products were examined at the peak of the low-temperature reaction curve at 760 mm. (402°), 1160 mm. (370°), and 1520 mm. (310°). The results are summarised in Table 4 (cols. 1—3) and show very similar amounts of reactants consumed in the three cases.

Oxidation of Propylene in Steel.—It was not considered safe to use the glass reactor above 2 atm. abs., and experiments were continued in the steel apparatus up to 4·5 atm. abs. Reaction–temperature curves for the 2 : 1 propylene–air mixture at 100-sec. residence are shown in Fig. 5. At atmospheric pressure, the low-temperature reaction is not in evidence, and the reaction curve is something like that in Pyrex glass with much shorter residence times, except that reaction sets in some 100° lower. At higher pressures reaction sets in about 300° and accelerates rapidly with rising temperature, but there is no indication of the " negative temperature coefficient " at higher temperatures.

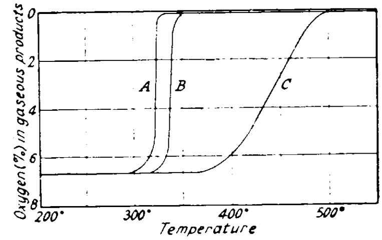


FIG. 6. *Variation in extent of reaction with rising temperature for* 2 : 1 *propylene–air mixture at various pressures* (*residence time of* 100 *sec. at* 20°; *steel reaction vessel*).

A, 4·5 *atm. abs.*
B, 3 *atm. abs.*
C, 1 *atm. abs.*

Further observations at atmospheric pressure with a descending reactor temperature showed that the " hysteresis " effect persisted in the steel vessel.

The products from experiments at 1 and 4 atm. abs. in which there was a reasonable amount of reaction at low temperature, are shown in Table 4 (last 2 cols.).

TABLE 4. *Products of reaction of* 2 : 1 *propylene–air mixture in Pyrex glass at* 100-*sec. residence time* (*measured at* 20° C) *and various pressures.*

Pressure (absolute)	760 mm.	1160 mm.	1520 mm.	1 atm.*	4 atm.*
Temp., ° C	402	370	310	440	345
% carbon as :					
unchanged C_3H_6	84	82	85	96	78
CO	1·3	1·0	1·2	0·2	1·0
CO_2	0·4	0·2	0·1	0·7	0·25
HCHO	1·3	1·1	1·3	nil	trace
higher aldehyde (as $CH_3 \cdot CHO$)	0·9	2·1	2·1	nil	0·9
C_4 hydrocarbons	1·3	1·4	5·9	trace	9·4
C_5 hydrocarbons	0·6	1·8	4·5		
C_6 hydrocarbons	—	0·4	—		
acid	0·1	trace	trace	nil †	nil †
deficiency	10	10	1·6 excess	3	10
% oxygen as :					
unchanged O_2	7	5	4	60	6·1
CO	19	15	18	2·7	17·2
CO_2	8	6	4	19·5	9·1
HCHO	20	16	16	nil	trace
higher aldehyde (as $CH_3 \cdot CHO$)	6	17	17	nil	9·1
acid	2·5	trace	trace	nil †	nil †
deficiency (incl. H_2O)	35	39	41	18	59

* In a steel reaction vessel. † Acid and peroxide.

DISCUSSION

Ethylene.—The present results invite comparison with those obtained by Lenher in his single-pass flow apparatus. Using ethylene : oxygen ratios similar to our own, Lenher conducted his experiments at lower temperatures but with longer residence times, so that the extent of reaction in the two cases is similar.

In contrast to Lenher we have found in the products : (1) a considerable proportion of higher olefins, especially propylene; (2) aldehydes, including formaldehyde, but no ethylene oxide; (3) a higher ratio of formaldehyde to formic acid; and (4) a higher ratio of carbon oxides to liquid products. With the exception of (4), these changes were also observed by Lenher when, in his recirculation experiments, reaction temperatures up to 600° were employed.

In the investigation of Newitt and Mene a 2 : 1 ethylene–air mixture was again employed, but the use of high pressures allowed the reactions to be conducted at relatively low temperatures. The reaction vessel was constructed of stainless steel. Under these conditions considerably more ethylene reacted than in our experiments, but the ratio $CO : CO_2$ was smaller. The liquid products, which included ethylene glycol, contained more formic acid and acetaldehyde relative to formaldehyde than we found. The most striking feature of the results of Newitt and Mene was however the high proportion (60—90%) of ethylene consumed which was not accounted in the products. The ratio of H : C in the missing material was generally about 2 and the obvious inference, in the light of the present work, is that it consisted chiefly of higher olefins.

Propylene.—Spontaneous ignition pressure–temperature limits for propylene–air mixtures containing up to 6% of the hydrocarbon have been determined by Kane and Townend (*Proc. Roy. Soc.*, 1937, *A*, **160**, 174) using a stainless-steel reaction vessel. Above about 500° ignition pressures increase smoothly with increasing temperature, but a point of inflection appears in the relation between 500° and 450°. In this range the present results, which refer to considerably richer mixtures reacting at atmospheric pressure in Pyrex glass, show a minimum overall reaction rate. The minimum disappears with weaker mixtures, but there is a general diminution in reactivity in this direction and, as Kane and Townend show, the ignition pressure also rises. It appears from our own results (Fig. 5) that maximum reactivity is reached at about the 67% propylene–air mixture. The more reactive mixtures show a maximum reaction rate at about 400°, but at higher pressures this temperature appears to fall and, one may suggest, tends towards the optimum temperature for cool flame formation found by Kane and Townend. The present work reveals also a tendency to a subsidiary rate-maximum at about 450°. This may be associated with a subsidiary lobe in the cool-flame limit of the type discussed by Malherbe and Walsh (*Trans. Faraday Soc.*, 1950, **46**, 835). The results observed are in accord with the view of these authors that the variations in rate of reaction of hydrocarbons with oxygen in the low-temperature range are explicable in terms of the varying point of attack by oxygen on the initially formed hydroperoxide to initiate chain branching. From propylene we should expect to get at first the peroxide $CH_2{:}CMe{\cdot}O_2H$. The favoured point of attack by oxygen would be the methylene group and to such a reaction may be attributed the principal peak in the reaction rate at about 400°. The embryonic peak at a somewhat higher temperature may denote parallel attack on the methyl group. At a higher temperature, or in the presence of an oxidised ferrous surface, the initial peroxide is decomposed as rapidly as it is formed and before there is time for appreciable attack by oxygen. In these circumstances the resultant branching reaction does not appear. Increase in pressure, however, even in the presence of an oxidisable surface, restores reaction at low temperature. The rate curves do not however reveal whether this reaction is of the same kind as that observed in Pyrex glass.

The analytical results given in Table 3 show that detectable amounts of peroxide survive when the low-temperature reaction is vigorous but not at temperatures above 450°. The survival of formaldehyde and carbon monoxide is favoured by rapid reaction in either temperature range, but especially the lower. A feature of the results is the appearance of considerable proportions of higher hydrocarbons in the products. In the Pyrex glass reactor, their survival is favoured by rapidity of reaction and by increase of pressure.

In the mild steel reactor the survival of intermediate products is greatly suppressed. It appears that the oxidisable ferrous surface promotes destructive oxidation of the oxygenated intermediates to carbon dioxide and water. It will be noted that with *stainless* steel, neither Lenher (with ethylene) nor Newitt and Mene (with ethylene and propylene) found such profound effects. To some extent however the destruction of intermediates, and presumably of the low-temperature combustion system, is offset by increase in pressure, whereby the concentration of gas molecules relative to the surface area is increased. Evidently the higher hydrocarbons are less easily attacked in the presence of oxidisable surface than are the aldehydes, with the consequence that their survival benefits the more from the pressure increase. It will be noted too that the ratio CO : CO_2, which falls off greatly when mild steel is substituted for Pyrex, is somewhat restored at the higher pressure.

In Newitt and Mene's experiments at still higher pressures and lower temperatures, rather greater proportions of oxygen were used. The tendency was, however, for rather less propylene to be oxidised, with the consequence that higher yields of oxygenated intermediates were obtained, including propylene oxide, propylene glycol, and glycerol in addition to the products found in the present work. As with ethylene, the substantial deficiency in their carbon balances was probably due chiefly to the higher hydrocarbons which, as our results show, can account for quite half of the propylene reacting.

We are indebted to the Distillers Company Limited for sponsoring this work. We have had the advantage of several discussions with members of the Company's Research and Development Department, particularly in connection with the polarographic oxygen indicator.

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