27. *Syntheses of* (1) *Glycerol and Propylene Glycol from Propylene, and* (2) *Ethylene Glycol from Ethylene.*

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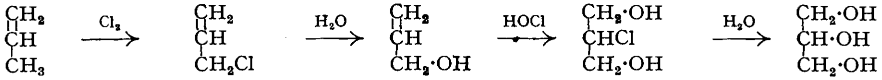
In the early stages of the slow combustion of an olefin at high pressures there is formed a mixture of the corresponding oxide and the isomeric aldehyde and alcohol. Under appropriate conditions of temperature and pressure the oxide is hydrolysed to glycol and the alcohol is further oxidised and hydrolysed to a polyhydric alcohol. For instance, propylene gives propylene glycol and glycerol, and ethylene gives ethylene glycol. The effect of temperature, pressure, and other factors on the course of the combustion is described.

Olefin hydrocarbons, available in large quantities from petroleum-cracking, are by virtue of their structure suitable starting materials for the syntheses of certain unsaturated and polyhydric alcohols and of glycols; as an example, glycerol may be prepared from propylene by first chlorinating it at a relatively high temperature (500°), hydrolysing the allyl chloride, and chlorhydrinating the resultant alcohol in aqueous solution (Williams, *Chem. and Met. Eng.*, Dec. 1940) :

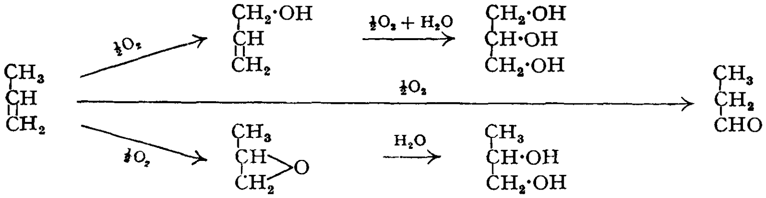


$$\begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_3\end{matrix} \xrightarrow{Cl_2} \begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2Cl\end{matrix} \xrightarrow{H_2O} \begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2{\cdot}OH\end{matrix} \xrightarrow{HOCl} \begin{matrix}CH_2{\cdot}OH\\ |\\ CHCl\\ |\\ CH_2{\cdot}OH\end{matrix} \xrightarrow{H_2O} \begin{matrix}CH_2{\cdot}OH\\ |\\ CH{\cdot}OH\\ |\\ CH_2{\cdot}OH\end{matrix}$$

In this series of changes allyl alcohol is produced by the addition of oxygen, and glycerol by the addition of water and oxygen, to the parent hydrocarbon, chlorine being the agent used for introducing hydroxyl groups into the molecule. We have found that a similar result may be brought about by simple homogeneous or heterogeneous oxidation and hydrolysis at elevated pressures with or without the presence of added water.

Under appropriate conditions of temperature, pressure, and oxygen concentrations olefins give initially, or in the early stages of their slow combustion, the corresponding oxides together with isomeric aldehydes and alcohols—the relative amounts of the three isomers surviving being determined, partly, by the experimental conditions. The homogeneous oxidation cannot, however, be entirely arrested at this point, and complex changes subsequently take place resulting in the formation of polyhydric alcohols, glycols, lower aldehydes, acids, the two oxides of carbon, and steam. If the oxygen present is insufficient for complete combustion, or if the reaction is curtailed, varying quantities of all the stable intermediate and final products of the oxidation survive and can be isolated and identified.

A detailed analysis of the condensable products from such an oxidation of propylene has revealed the presence of appreciable amounts of propaldehyde, propylene glycol, and glycol, the last two apparently having been formed by secondary reactions from propylene oxide and allyl alcohol, respectively, according to the following scheme :



$$\begin{matrix}CH_3\\ |\\ CH\\ \|\\ CH_2\end{matrix} \xrightarrow{\frac{1}{2}O_2} \begin{matrix}CH_2{\cdot}OH\\ |\\ CH\\ \|\\ CH_2\end{matrix} \xrightarrow{\frac{1}{2}O_2 + H_2O} \begin{matrix}CH_2{\cdot}OH\\ |\\ CH{\cdot}OH\\ |\\ CH_2{\cdot}OH\end{matrix}$$

$$\begin{matrix}CH_3\\ |\\ CH\\ \|\\ CH_2\end{matrix} \xrightarrow{\frac{1}{2}O_2} \begin{matrix}CH_3\\ |\\ CH_2\\ |\\ CHO\end{matrix}$$

$$\begin{matrix}CH_3\\ |\\ CH\\ \|\\ CH_2\end{matrix} \xrightarrow{\frac{1}{2}O_2} \begin{matrix}CH_3\\ |\\ CH\\ |\\ CH_2\end{matrix}\!\!>O \xrightarrow{H_2O} \begin{matrix}CH_3\\ |\\ CH{\cdot}OH\\ |\\ CH_2{\cdot}OH\end{matrix}$$

Ethylene behaves similarly, the initial stable products of its oxidation being ethylene oxide and acetaldehyde; vinyl alcohol may also, possibly, be formed, although attempts to isolate it have hitherto proved unsuccessful (Bone *et al.*, *Proc. Roy. Soc.*, **1933**, *A*, **143**, 16). At high pressures and in the presence of steam the oxide is almost completely converted into ethylene glycol.

Although the present communication does not deal with the catalytic combustion of the olefins, it will be recalled that highly selective catalysts are known which will arrest the oxidation of ethylene and propylene at an early stage; giving high yields of the corresponding oxide or glycol.

EXPERIMENTAL.

To study experimentally slow-combustion processes over a wide pressure range it is necessary to resort to metal reaction vessels and auxiliary equipment, and the results may, therefore, be modified to some extent by surface reactions preceding or taking place concurrently with gas-phase reactions. In the present instance, however, it has been shown that such surface effects are small, and lining the reaction chamber with copper or silica, or partly filling it with steel shavings, does not appear to alter appreciably the general character of the combustion.

The apparatus employed is similar to that previously described (J., 1937, 1666). The hydrocarbon and air or oxygen are stored separately under pressure in steel cylinders; they are introduced directly into the reaction vessel through a fine-adjustment inlet valve, the quantities being determined by measuring their respective partial pressures. The cylindrical reaction vessel is fabricated of an austenitic stainless steel and has a capacity of *ca.* 500 c.c.; it is completely enclosed in an electric furnace so wired as to compensate for the large end losses. Temperatures are measured by a platinum–rhodium thermocouple placed in a thin-walled, steel pocket traversing axially the reaction chamber.

In carrying out a typical experiment, the reaction vessel is first heated to the desired temperature, evacuated, and the requisite amounts of hydrocarbon and oxygen or air admitted separately through the inlet valve. The course of the reaction may then be followed by analysing samples withdrawn at suitable intervals or, in some instances, by observing the temperature changes in the vessel. At the conclusion of reaction or at any pre-selected time, the contents of the vessel are released through the outlet valve, the condensable and the water-soluble products being separated and collected in a train of cooling coils and scrubbers, and the gaseous products sampled and metered. The methods employed in the analysis of the products are described later.

The propylene used was purchased in cylinders from the Ohio Co. of America and, by analysis, was found to contain 99·5% of the hydrocarbon. A cylinder of specially purified ethylene was purchased from the British Oxygen Co. and found to contain 99·7% of the hydrocarbon. Both gases were used without further purification.

The Slow Oxidation of Propylene.—When a propylene–oxygen mixture containing excess of the hydrocarbon is raised to such a temperature that reaction ultimately will occur, there is a time "lag" during which no detectable change takes place, followed by a period of uniform slow combustion during which the greater part of the oxygen is consumed. As the temperature is progressively raised, the "lag" shortens and the subsequent reactions speed up until eventually the medium becomes self-heating and ignition may occur. In all the experiments described below, however, the conditions (unless otherwise stated) are such as to ensure substantial constancy of temperature. In general, upwards of 90% of the oxygen is used up, about 60% appearing in the products as condensable vapours (including water) and the remainder as the two oxides of carbon. In the tabulated results the yields are expressed as percentages of the total oxygen in the initial mixture appearing as oxides of carbon, and percentages of the total oxygen in the condensable products appearing as total aldehydes, total acids, propylene glycol, and glycerol.

In Table I the data for various propylene–oxygen and air media reacting at temperatures between 215° and 260° are summarised. In all cases the partial pressure of the hydrocarbon in the initial mixture is 8 atm. and those of the oxygen and nitrogen are as stated.

TABLE I.

Products from the Reaction of Various Propylene–Oxygen (*or Air*) *Media at Temperatures between* 215° *and* 260°.

(Partial pressure of propylene = 8 atm.)

Initial mixture, $C_3H_6 : O_2 : N_2$.	Total press., atm.	Reaction temp.	% of total oxygen appearing in products as:		% of oxygen in condensable product appearing as:				
			CO_2.	CO.	Total aldehydes.	Total acids.	Propylene oxide and glycol.	Glycerol.	By diff. (mainly H_2O).
4 : 3 : 0	14	215°	30·2	8·1	7·4	20·5	1·1	2·2	68·8
4 : 2 : 0	12	215	29·1	6·9	11·0	13·2	2·2	4·9	68·7
4 : 1 : 0	10	215	36·5	5·9	16·0	12·3	4·6	7·4	59·7
4 : 1 : 0	10	250	33·9	7·5	16·7	5·9	3·6	6·5	67·3
4 : 1 : 3·8	17·6	230	30·2	8·8	16·4	9·4	11·8	4·1	58·3
		250	26·5	13·3	16·8	6·2	8·8	4·3	63·9
		260	20·8	22·3	20·0	2·3	5·5	4·2	68·0

Considering first the propylene–oxygen experiments, it will be observed that the yields of those products which are formed in the early stages of the combustion, *viz.*, the aldehydes, glycol, and glycerol, increase with the concentration of the hydrocarbon, whilst the acids formed at a later stage diminish. For instance, by increasing the propylene from 57% to 80% the yield of total aldehydes is doubled, that of glycerol more than trebled, and that of glycol increased four-fold. The effect of increasing the reaction temperature of the 4 : 1 mixture from 215° to 250° is to diminish the yields of acids, glycol, and glycerol and slightly to increase that of the total aldehydes. In all the experiments included in this series, from one-third to one-half of the total aldehyde content of the products consists of formaldehyde, whilst some 80% of the gaseous products consists of carbon dioxide. No free hydrogen is found amongst the gases.

The influence of temperature upon the course of the combustion may best be seen by reference to the data for the 4 : 4·8 propylene–air mixtures. The temperature range covered is from 230°, at which the reaction is comparatively slow, to 260°, at which it is rapid and is accompanied by a slight rise of temperature. On progressively increasing the temperature from 230° the yields of glycol and total acids diminish rapidly, the glycerol remains fairly constant, whilst the total aldehydes increase; the ratio CO_2/CO diminishes until at 260° the two oxides are present in approximately equal amounts.

Since the formation of glycol and glycerol involves hydrolysis, it was thought that the addition of water vapour to the reacting medium might increase the yields of both these products; accordingly, a series of experiments was carried out, comparable with the propylene–air series but with the nitrogen replaced by an equivalent quantity of steam. The results are given in Table II.

TABLE II.

Products from the Reaction of a 4 : 1 : 3·8-*Propylene–Oxygen–Steam Medium at Various Temperatures between* 240° *and* 280° *and at* 17·6 *Atmospheres Pressure.*

Reaction temp.	% of total oxygen appearing in products as:		% of oxygen in condensable products appearing as:				
	CO_2.	CO.	Total aldehydes.	Total acids.	Propylene oxide and glycol.	Glycerol.	By diff. (mainly H_2O).
240°	22·9	7·4	14·4	8·7	4·9	6·2	65·8
258	23·6	13·0	26·0	3·8	7·7	6·5	56·0
269	43·6	16·2	35·5	9·8	19·7	11·2	23·8
280	35·0	10·2	33·5	6·9	10·3	14·4	34·9

The immediate effect of this replacement is to slow down the combustion, and consequently somewhat higher temperatures have to be employed to obtain reaction rates comparable with those of the air series. The general effect is to favour the formation and survival of the initial products of combustion and hydrolysis. For instance, the yield of total aldehydes reaches a maximum of 35·5%, propylene oxide and glycol 19·7%, and glycerol 14·4%. A rapid rate of reaction also seems to favour their survival.

The Slow Oxidation of Allyl Alcohol and Propylene Glycol.—The three isomeric compounds (propylene oxide, allyl alcohol, and propaldehyde) which are found in the early stages of propylene oxidation may be formed simultaneously as a result of intermolecular changes from an initially formed propylene–oxygen complex, or they may owe their origin to the specific nature of the oxygen attack, their formation depending upon such factors as the orientation of the reacting molecules at the moment of collision, the concentration of hydrocarbon, and the temperature. Our experiments do not enable a distinction to be drawn between these possibilities. It is easy to show, however, that whereas propylene glycol results from the hydrolysis of the oxide, glycerol is formed solely by the oxidation and hydrolysis of allyl alcohol. For example, a 2 : 5 allyl alcohol–air medium at 14 atm. reacts at 230° and upwards, ignition occurring at 270°. The products consist of aldehydes, acids, glycerol, the two oxides of carbon, and steam; at 235° about 23% of the carbon of the alcohol burnt appears as total aldehydes, and 4% as glycerol. Under similar conditions neither propylene glycol nor propaldehyde gives glycerol, the products of the reaction of the former being aldehydes and acids and those of the latter being peroxide compounds, alcohols, lower aldehydes, and acids (J., 1939, 1717).

The Slow Oxidation of Ethylene.—The products from the slow oxidation of ethylene are less numerous than in the case of propylene, and the influence of temperature and pressure on the course of the combustion is easier to determine. A 2 : 1-ethylene–air medium at pressures of 10 atm. and upwards will react at a temperature as low as 200°, giving acetaldehyde and formaldehyde, ethylene glycol, acetic and formic acids, the two oxides of carbon, and steam. In certain circumstances small amounts of methyl and ethyl alcohols, formed by secondary reactions, are also found, but little or no ethylene oxide.

The results of three series of experiments with a 2 : 1 ethylene–air mixture at 30, 68, and 100 atm. and over a temperature range giving at one extremity very slow isothermal combustion and at the other rapid combustion with self-heating, are summarised in Table III.

TABLE III.

Products from the Reaction of a 2 : 1-*Ethylene–Air Medium at* 30, 68, *and* 100 *Atm. Pressure and at Various Temperatures.*

Reaction temp.	% of total oxygen appearing in products as:		% of oxygen in condensable product appearing as:				
	CO_2.	CO.	H·CHO.	CH_3·CHO.	Ethylene glycol.*	Acetic and formic acids.	By diff. (mainly H_2O).
			Initial pressure :	30 atm.			
237°	40·8	32·0	31·6	35·6	1·5	23·6	7·7
246	32·3	35·8	20·2	20·0	8·7	16·8	34·3
276	32·5	29·1	21·8	13·8	21·0	10·3	33·1
			Initial pressure :	68 atm.			
221	31·3	37·1	9·8	4·1	8·7	56·0	21·4
230	31·8	19·1	4·4	3·7	7·4	31·0	53·5
252	28·9	25·6	4·1	9·7	18·2	15·8	52·2
255	26·1	31·8	6·6	15·2	13·4	21·1	43·7
			Initial pressure :	100 atm.			
209	28·9	22·3	1·9	5·3	19·0	29·7	44·1
215	26·3	24·3	1·5	6·6	21·2	18·2	52·5
226	26·3	26·3	1·3	7·1	26·8	17·3	47·5
236	30·7	30·7	1·2	9·4	40·6	17·3	31·5

* Contains only traces of ethylene oxide.

It will be seen that by increasing the initial pressure of the reacting medium the yields of ethylene glycol are increased whilst those of both formaldehyde and acetaldehyde are diminished. The effect of increasing the reaction temperature, at constant pressure, is to increase the yields of glycol and to diminish those of acetic and formic acids. At 30 atm. the yields of the two aldehydes diminish, whereas at higher pressures they tend to increase with increasing temperature. The ratio CO_2/CO shows no marked variation with temperature or pressure.

The effect of replacing the nitrogen of the air by steam is shown in Table IV. At 68 atm. the amounts of glycol surviving in the products are considerably increased, whilst the corresponding figures for the acids show a marked diminution. The aldehydes do not appear to be much affected by the substitution of steam. The ratio CO_2/CO, which has a value of about unity for the ethylene–air mixtures, increases to 3—4 for the steam-diluted mixtures.

TABLE IV.

Products from the Reaction of a 9 : 1 : 3·8-*Ethylene–Oxygen–Steam Medium at* 68 *Atm. and at Various Temperatures.*

	% of total oxygen appearing as :		% of oxygen in condensable products appearing as :					
Reaction temp.	CO_2.	CO.	H·CHO.	CH_3·CHO.	Ethylene glycol.*	Acetic and formic acids.	EtOH.	By diff. (mainly H_2O).
222°	49·1	13·0	6·0	9·8	20·6	18·1	12·6	32·9
241	36·3	8·1	6·4	4·2	17·4	5·0	9·9	57·1
256	37·0	10·2	3·4	4·8	18·6	4·4	6·2	62·6

* Contains only traces of ethylene oxide.

In all the ethylene experiments some polymerisation of the hydrocarbon to a brownish oil takes place.

Analytical.—The methods of identifying and estimating aldehydes, alcohols, and acids have been described in previous papers (Newitt and Thornes, J., 1937, 1656; Newitt and Baxt, J., 1939, 1711).

Ethylene glycol was oxidised by acid potassium permanganate to glyoxal, which was identified by the Bamberger test and by preparing the dinitrobenzoate.

Propaldehyde was oxidised to oxalic acid by means of potassium permanganate, and the acid reduced by zinc and hydrochloric acid to glyoxylic acid. On addition of phenylhydrazine hydrochloride and potassium ferricyanide a red colour is produced (Paget and Berger, *J. Pharm. Chim.*, 1938, **8**, 577; McNair, *J. Amer. Chem. Soc.*, 1932, **54**, 3249).

Ethylene oxide and propylene oxide give a pink precipitate on addition of a saturated, neutral solution of manganese chloride (Lenher, *ibid.*, 1931, **53**, 3737). They were estimated quantitatively by a method due to Lubath (*Chem. and Ind.*, 1932, **51**, 361), which involves the addition of hydrochloric acid to the oxide.

Glycerol was detected by converting it into dihydroxyacetone, which gives a characteristic indigo-blue ring on adding concentrated sulphuric acid and a 1% alcoholic solution of veratrole (Arreguine, *Anal. Asoc. Quim. Argentina*, 1936, 24). Its presence was confirmed by preparing the tribenzoate. The quantitative estimation was carried out by the method described by Malaprade (*Bull. Soc. chim.*, 1937, **4**, 906). The solution containing glycerol was exactly neutralised (pale-yellow tint) with methyl-red as indicator, an excess of sodium periodate solution was added, and the mixture set aside for 20 mins. A concentrated solution of potassium nitrate was added, and the appearance of a white precipitate of potassium periodate indicated the presence of an excess of the sodium salt. The resulting solution, which was acid, as shown by the red colour of the indicator, was titrated against standard sodium hydroxide to the original yellow tint. The reaction is $2NaIO_4 + C_3H_8O_3 = 2H{\cdot}CHO + H{\cdot}CO_2H + 2NaIO_3 + H_2O$, 1 equiv. of glycerol giving 1 equiv. of formic acid.

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