[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

THE DECOMPOSITION OF ETHYLENE GLYCOL IN THE PRESENCE OF CATALYSTS. I. VANADIUM PENTOXIDE AS CATALYST

BY NATHAN L. DRAKE AND THOMAS B. SMITH[1]

RECEIVED AUGUST 22, 1930 PUBLISHED NOVEMBER 5, 1930

The generation of an ethylene oxide linkage by the direct addition of oxygen to a double bond would be a useful reaction. In particular, starting from ethylene, it would be easy to prepare ethylene glycol

$$2CH_2{=}CH_2 + O_2 + 2H_2O = 2CH_2OHCH_2OH \qquad (1)$$

Francis[2] has calculated an expression for the free energy of formation of ethylene from its elements

$$\Delta F = 12{,}260 + 11.6T$$

and Parks and co-workers[3] have revised their earlier calculations of the free energy of formation of liquid ethylene glycol, giving as their revised value

$$\Delta F_{298} = -81{,}800 \text{ cal.}$$

From Francis' equation, for ethylene

$$\Delta F_{298} = +15{,}717 \text{ cal.}$$

For liquid water[4]

$$\Delta F_{298} = -56{,}560 \text{ cal.}$$

Consequently, for the reaction

$$CH_2{=}CH_2(g) + {}^1/_2O_2(g) + H_2O(l) = CH_2OHCH_2OH(l)$$
$$\Delta F_{298} = -40{,}957 \text{ cal.}$$

There is, therefore, nothing thermodynamically unsound in an attempt to devise a method for carrying out this reaction. The use of pressure would certainly aid much in bringing about Reaction 1, and if a catalyst could be found which would render possible the production of ethylene oxide, the synthesis of glycol from ethylene, air and water should be possible.

Obviously the simplest method of testing a number of catalysts would be to examine their effect on the decomposition of ethylene glycol under various conditions. The present paper is concerned with the beginning of such a study. This method of attack permits operation at ordinary pressure in simple apparatus, and is undoubtedly the most economical of time and

---

[1] From a thesis presented by T. B. Smith to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Master of Science.

[2] Francis, *Ind. Eng. Chem.*, **20**, 279 (1928).

[3] Parks and co-workers, THIS JOURNAL, **51**, 1969 (1929).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 607.

material. A gas analysis of the products of decomposition enables the operator to follow very easily the course of the decomposition.

Practically no work has been done on the influence of catalysts on ethylene glycol. Sabatier[5] found that glycol passed over alumina at 400° yielded chiefly acetaldehyde which polymerized partially to paraldehyde. Trillat[6] passed glycol over a platinum spiral at 90° and noted that the spiral was raised to incandescence, with decomposition of the glycol into formaldehyde, glycolic aldehyde and glyoxal.

The extended use of vanadium pentoxide as an oxidation catalyst led the authors to choose it for use in their preliminary studies. There is no reported work on the influence of vanadium pentoxide on ethylene glycol.

Preparation and Purification of Materials.—The catalyst used in these investigations was prepared from ammonium vanadate. Fused vanadium pentoxide was treated with hot concentrated (sp. gr. 1.42) nitric acid, about 150 cc. of acid for each 5 g. of vanadium pentoxide, and the solution filtered and evaporated nearly to dryness. The product separating from the solution during evaporation was filtered off, washed twice with cold distilled water to remove the greater part of the acid and dissolved in concentrated aqueous ammonia (sp. gr. 0.90). The resulting solution was again filtered and nearly saturated with ammonium nitrate which had been recrystallized from water. The solution was then allowed to stand for a period of twelve hours to allow crystallization of the ammonium metavanadate to take place. This material was dissolved in dilute aqueous ammonia and again caused to crystallize as above. The ammonium metavanadate so prepared was filtered from the solution, washed once with cold water and dried over calcium chloride in a vacuum.

The catalyst used in the decomposition studies was obtained by heating in a stream of oxygen 0.5 g. of ammonium vanadate contained in a small porcelain boat. The temperature of the furnace in which the boat was heated was raised slowly to 350°, and maintained there until no trace of ammonia could be detected issuing from the furnace. Matignon[7] has shown that vanadium pentoxide is produced from ammonium metavanadate only in this way. If the metavanadate is not heated under oxidizing conditions, a substance of the composition $5V_2O_5{\cdot}2VO_3NH_4$ results. Some preliminary experiments described below were conducted with this substance as the contact material.

The ethylene glycol used was obtained by carefully distilling commercial ethylene glycol, called Prestone, and collecting the fraction boiling at 197°.

Apparatus

The apparatus used is shown in Fig. 1: G, a pyrex tube, containing the ethylene glycol, was heated by means of the oil-bath H, whose temperature was maintained at 205° by a Bunsen burner protected from drafts by an asbestos shield. Glycol was introduced by means of a capillary into G through I, which was then closed by a piece of glass rod and a short piece of tightly fitting rubber tubing. Connecting G with the furnace F was a small capillary orifice M, electrically heated to 200°. Glycol vapor generated in G under slight pressure, passed through this orifice at a constant rate into the furnace F. The latter consisted of a 16 × 250-mm. pyrex tube fitted snugly into

---

[5] Sabatier, "Catalysis in Organic Chemistry," translated by Reid, D. Van Nostrand Co., New York, **1922**, pp. 234, 240.

[6] Trillat, *Bull. soc. chim.*, [3] **29**, 35 (1903).

[7] Matignon, *Chem.-Ztg.*, **75**, 986 (1905).

another of 20 mm., the larger tube wound with chromel ribbon for electrically heating the reaction chamber. A 35-mm. tube wrapped with asbestos sheet enclosed the reaction chamber. By means of a lamp-bank the temperature in the furnace could be regulated at will. The thermometer projected into the reaction chamber to within a few mm. of the porcelain boat containing the catalyst. E, a coil condenser, which was cooled in an ice- and salt-bath during the experiments, was provided with a condensate trap and connected to the low head scrubber D. The scrubber had a volume of 300 cc. and contained 4 N magnesium sulfate solution. The scrubber was connected by means of the ground-glass joint in the tube C to a gasometer B, which was provided with a tenth degree thermometer, a mercury manometer, A, an outlet tube and a connection to the analyzer. The volume of gas contained in B could be read off directly by means of graduations marked on the gasometer.

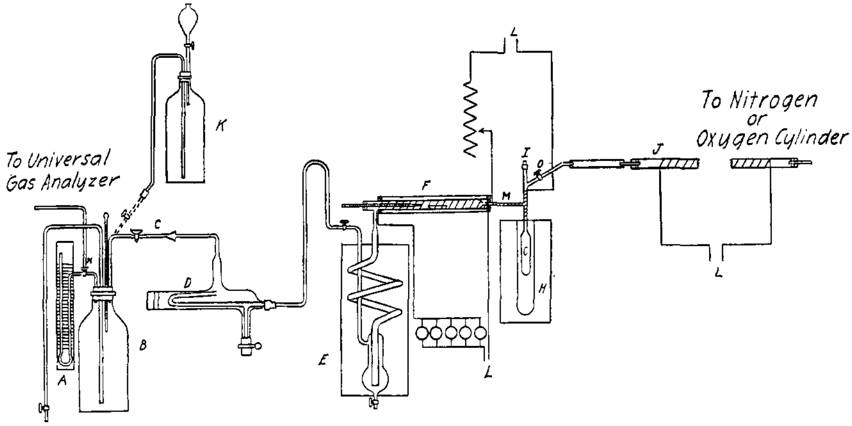


Fig. 1.—*A*, Manometer; *B*, gasometer; *C*, movable tube; *D*, scrubber; *E*, condenser; *F*, reaction furnace; *G*, glycol vaporizing bulb; *H*, crisco bath; *I*, bulb inlet; *J*, nitrogen purifier; *K*, aspirator; *L*, to 110-volt line.

The catalyst was introduced or removed through the left end of the reaction furnace, after removing the thermometer with its accompanying stopper. The products of decomposition together with the undecomposed glycol passed into the condenser, where the glycol, water and the major portion of the acetaldehyde were removed. The remainder of the acetaldehyde was removed in the scrubber. By means of the stopcock on the siphon from the gasometer, the pressure within the system from gasometer to capillary orifice could be maintained very near to atmospheric.

At the conclusion of an experiment, the tube C was disconnected at the ground joint and attached to the magnesium sulfate reservoir K. This reservoir supplied magnesium sulfate solution to replace the gas withdrawn for analysis, thus making it possible to store the gas at approximately atmospheric pressure. A Fisher Universal Gas Analyzer was used for the analytical work.

The apparatus used in fractionating the condensate consisted of a modified Claisen flask with a fractionating side arm, provided with a thermometer and connected to a small coil condenser which was cooled in an ice and salt mixture. The end of the condenser extended several centimeters below the surface of ice water contained in a 100-cc. Erlenmeyer flask.

Method.—0.5000 g. of ammonium metavanadate (equivalent to 0.3889 g. of V_2O_5) was placed in a small porcelain boat in the reaction chamber and converted into pentoxide as described above. Meanwhile, 0.1060 mole of glycol was run into the bulb G, and the reduced copper in the furnace J heated to 250°. The scrubber was filled with 4 N magnesium sulfate and the gasometer disconnected at the ground-glass joint. The system was then flushed out with nitrogen and connection again established with the gasometer. At this point gasometer and tube C were filled with the confining liquid and connected to the scrubber by means of the ground-glass joint. With the system thus prepared for collecting the reaction products, the temperature of the oil-bath H was raised to 205° and maintained there until the glycol had been vaporized completely from the container. Throughout the experiment the stopcock of the siphon tube of the gasometer was so adjusted that a 10-mm. pressure was maintained within the system. Approximately two hours was required to vaporize the glycol, whereupon a stream of nitrogen was again blown through the apparatus to sweep out the remainder of the reaction products. When approximately 1200 cc. of nitrogen had passed through the apparatus, the stopcock in C was closed and the gasometer disconnected. The catalyst was allowed to cool in a stream of nitrogen before it was removed.

Analytical Methods.—The gaseous decomposition products were analyzed in a Fisher Universal Gas Analyzer; carbon dioxide, oxygen, ethylene, carbon monoxide, hydrogen and methane were determined in the order mentioned. Successive analyses were run until the results checked to within 0.3%. Ethylene was determined by absorption in 24% fuming sulfuric acid, but a check determination was run by absorbing the gas in bromine water to confirm the results obtained by the sulfuric acid method.

In the aqueous condensate were found acetaldehyde, acetic acid and undecomposed glycol. The major portion of the acetaldehyde was slowly distilled from the mixture in the apparatus described above and collected in approximately 100 cc. of water contained in the receiver. This receiver was then replaced by another and the remaining aldehyde, the acetic acid and water were distilled into it. The Claisen flask was then weighed and the glycol distilled *in vacuo*. The distillation flask was reweighed to determine the weight of glycol distilled.

The acetaldehyde in the first portion of the distillate was determined as follows:[8] 0.5 g. of hydroxylamine hydrochloride was added to a 250-cc. portion and the resulting solution allowed to stand for thirty minutes, whereupon the hydrochloric acid liberated was titrated with $N/4$ alkali using tetrabrom phenol blue as indicator.[9]

The second fraction was analyzed as follows. The acetic acid was titrated with $N/4$ alkali, using phenolphthalein as indicator. In another portion the aldehyde was oxidized to acetic acid by alkaline hydrogen peroxide (3%), and the excess alkali was titrated with $N/4$ hydrochloric acid using phenolphthalein as indicator.[10] The difference between the amounts of acetic acid found in the two operations enables one to calculate the amount of aldehyde present in the mixture.

Any aldehyde contained in the scrubber was driven off and collected, using the same distillation apparatus as above. The amount of aldehyde in the distillate was determined by the hydroxylamine method.

Discussion of Results

By means of a carbon balance, the percentage of glycol which was decomposed on passing over the catalyst was calculated. Curve I, Fig. 2, represents graphically the results of such a calculation. The error in-

---

[8] Allen's "Commercial Organic Analysis," pp. 124–140, Vol. I; original method, *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, **42**, 81 (1921).

[9] Harden and Drake, THIS JOURNAL, **51**, 2278 (1929).

[10] Hoepner, *J. Soc. Chem. Ind.*, **38**, 735 (1919).

volved in this method of computing percentage of glycol decomposed is far less than would be the case if the recovered glycol were taken as a basis for the computation. In the region between 297 and 357°, the slope of the curve is large, but below and above these points the slope decreases. Evidently, from the slope of Curve I, there is little to be gained by operating at temperatures above 400°. With the apparatus described, operation at temperatures above 400° was impossible, but the apparatus has been redesigned and we will be able in the near future to continue the curve in the region above 400°.

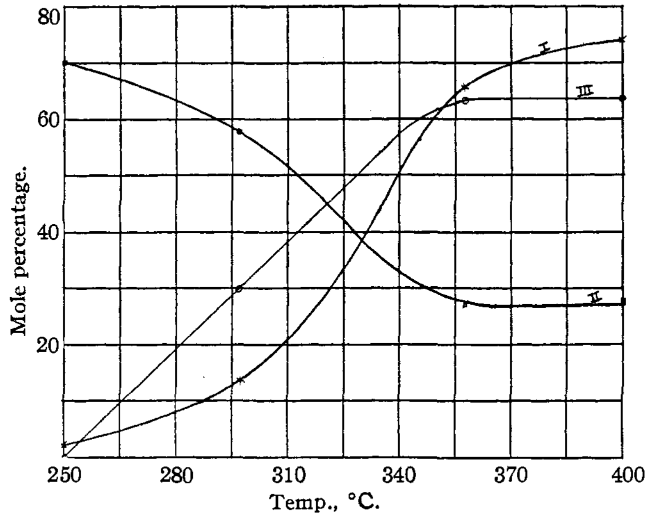


Fig. 2.—Decomposition of glycol in mole per cent. as a function of temperature.

The curves of Fig. 3 show the relation between the mole percentages of the various carbon-containing reaction products. It is very interesting and significant to note that up to a temperature of about 317°, more ethylene than any other product was produced. At 297°, for example, 7.75% of the total glycol was converted into ethylene. Referring to Fig. 2, however, we see that at this temperature 13.4% only of the glycol passing over the catalyst was decomposed. Consequently 58% of the *decomposed* glycol was converted into ethylene. Curves II and III of Fig. 2 show the relative percentages of ethylene and acetaldehyde formed, based on the glycol decomposed. It is more clearly evident from a consideration of these curves that nothing is to be gained by operation at a higher temperature. The curves for aldehyde and ethylene reach a maximum and a minimum, respectively, in the neighborhood of 357°, although the percentage of glycol decomposed increases nearly 10% between 357 and 400°.

During each experiment considerable reduction of the vanadium pentoxide took place, as shown by a color change from brick red to jet black. In the experiments from which the data for the curves of Figs. 2 and 3 were obtained, fresh catalyst was used at each temperature. That reduction of the oxide caused a considerable variation in the nature of the decomposition products was shown by using a specimen of catalyst a second time. These two experiments were conducted at a temperature of 360° in the usual fashion; the products formed are given in moles.

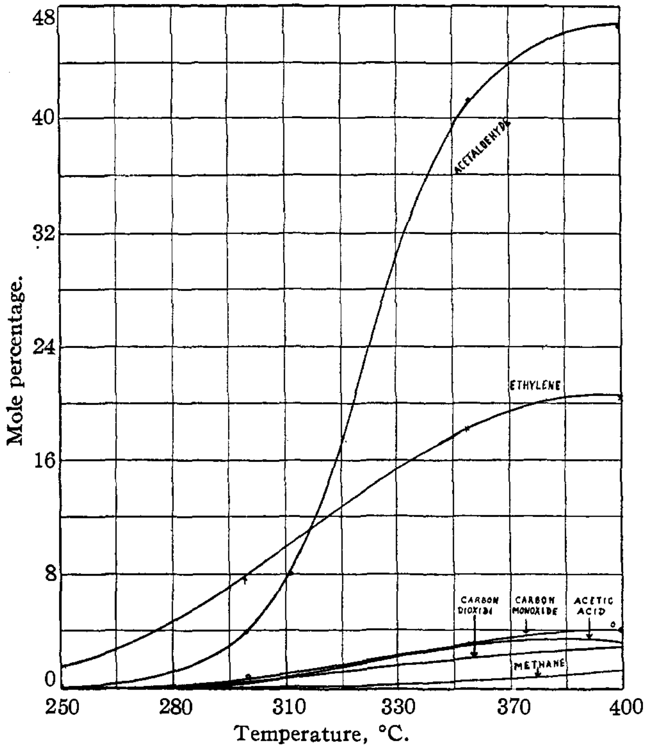


Fig. 3.—Percentage of total glycol used decomposed into acetaldehyde, ethylene, carbon monoxide, carbon dioxide, methane and acetic acid.

	I	II
CO_2	0.0045	0.0023
C_2H_4	.0196	.0145
CO	.0071	.0044
CH_3CHO	.0440	.0436
CH_3COOH	.0033	.0019

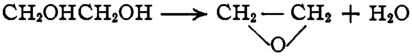
Evidently ethylene formation was more favored by the presence of fresh vanadium pentoxide than by the used catalyst, but either contact mass produced acetaldehyde in about equivalent amounts.

Two mechanisms are suggested to account for the production of aldehyde

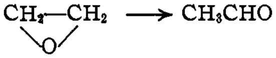
$$\mathrm{CH_2OHCH_2OH \longrightarrow CH_2{=}CHOH + H_2O} \tag{2}$$

$$\mathrm{CH_2{=}CHOH \longrightarrow CH_3CHO} \tag{3}$$

and

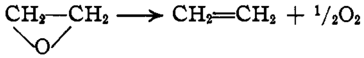


$$\mathrm{CH_2OHCH_2OH \longrightarrow \underset{\diagdown O \diagup}{CH_2{-}CH_2} + H_2O} \tag{4}$$



$$\mathrm{\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow CH_3CHO} \tag{5}$$

Ipatiev[11] has studied the behavior of oxides on heating both in the presence and absence of catalysts. Ethylene oxide passed through a glass tube was found to begin to decompose at 500°. In the presence of aluminum oxide, however, rearrangement of the oxide into acetaldehyde took place readily between 200 and 300°. The work of Nef[12] confirms in a general way that of Ipatiev. Nef observed a *slow* rearrangement of ethylene oxide into acetaldehyde in glass tubes at 400–420°. No evolution of gas took place in this temperature interval. The behavior of many substituted ethylene oxides on heating has been studied by Tiffeneau and Lévy[13] and Lévy and Sfiras.[14] Many of the oxides investigated undergo a rearrangement like that of ethylene oxide into acetaldehyde. This rearrangement, therefore, is common to α-oxides, and it is possible, consequently, that ethylene oxide was the intermediate from which both acetaldehyde and ethylene were formed. The following reaction would account for the ethylene



$$\mathrm{\underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow CH_2{=}CH_2 + {}^1/_2O_2} \tag{6}$$

The acetic acid is undoubtedly formed by the oxidation of acetaldehyde, and it will be seen that the contour of the acetic acid curve follows roughly that of the aldehyde curve, a condition to be expected if the acid is produced from aldehyde by oxidation.

For the production of carbon monoxide, two mechanisms are possible, and probably monoxide is formed through both. It is known that vanadium pentoxide acts as a dehydrogenation catalyst[15] and the reactions

$$\mathrm{CH_2OHCH_2OH \longrightarrow CHOCHO + 2H_2} \tag{7}$$

$$\mathrm{CHOCHO \longrightarrow 2CO + H_2} \tag{8}$$

readily account for the formation of carbon monoxide. It has also been

---

[11] Ipatiev, *Ber.*, **36**, 2016 (1903).

[12] Nef, *Ann.*, **335**, 201 (1904).

[13] Tiffeneau and Lévy, *Bull. soc. chim.*, **39**, 763–82 (1926).

[14] Lévy and Sfiras, *Compt. rend.*, **184**, 1335 (1927).

[15] Walker, British Patent 295,356 (1929); *C. A.*, **23**, 2186 (1929); Brown, U. S. Patent 1,757,830 (May 6, 1930); E. I. du Pont de Nemours and Co., British Patent 323,713 (March 5, 1930).

shown[16] that at elevated temperatures acetaldehyde readily decomposes according to the equation

$$CH_3CHO = CO + CH_4 \quad (9)$$

This reaction accounts not only for the presence of carbon monoxide, but also predicts the simultaneous formation of methane in equivalent amount. Although the methane curve of Fig. 3 follows roughly in shape those for carbon monoxide and acetaldehyde, the methane found was always considerably less than would correspond to the carbon monoxide. It is probable therefore, that Reactions 8 and 9 were each responsible for some carbon monoxide, and that the methane is produced according to 9. A small amount of hydrogen was always found in the gases. Undoubtedly most of the hydrogen formed was oxidized to water by the catalyst, but the presence of a small amount of it is evidence that Reactions 7 and 8 took place to some extent.

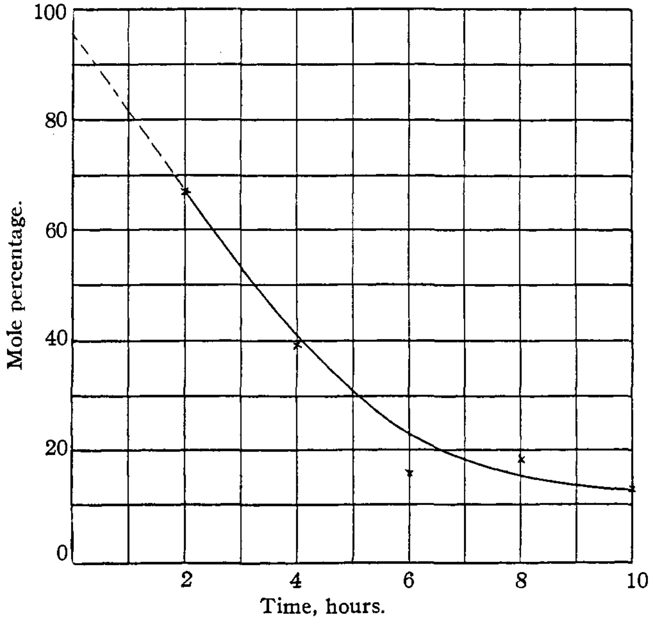


Fig. 4.—Decomposition of glycol in mole percentage plotted as a function of catalyst aging expressed in hours (temperature, 360°).

The carbon dioxide and carbon monoxide curves have the same shape, the former below the latter. Oxidation of carbon monoxide is without doubt the mechanism by which the dioxide is formed.

Figures 4 and 5 represent a series of preliminary experiments in which the compound described by Matignon[7] was used as catalyst. It will be noted that the amounts of the various products formed become rapidly less as

---

[16] Peytral, *Bull. soc. chim.*, **27**, 34–39 (1929); Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **111A**, 380 (1926).

the catalyst ages. How much of this effect is due to change in physical structure of the catalyst and how much to reduction it is impossible to say. With this contact mass even the acetaldehyde concentration decreased rapidly as the catalyst aged, a situation not paralleled when vanadium pentoxide was used.

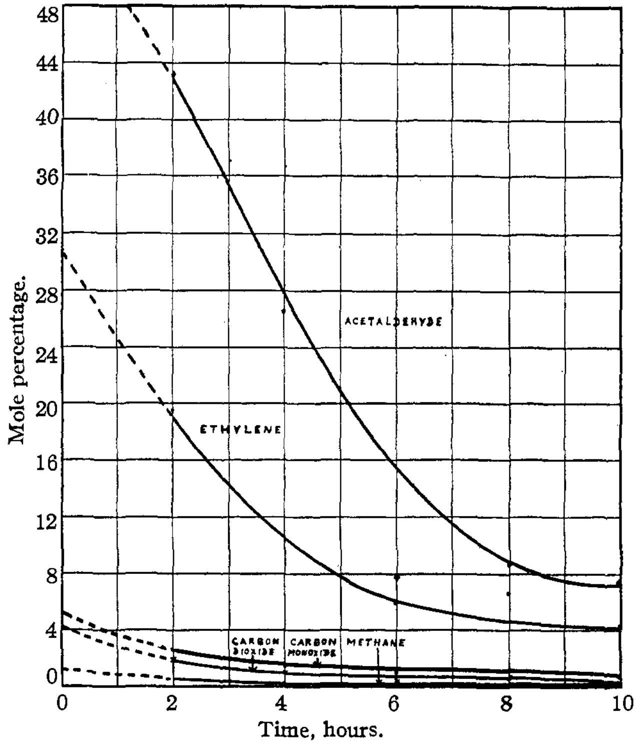


Fig. 5.—Acetaldehyde, ethylene, carbon dioxide, carbon monoxide, and methane as mole percentage of glycol used plotted as a function of the catalyst aging expressed in hours (temperature, 360°).

If the two hour points on the curves of Figs. 4 and 5 are compared with the corresponding points on Figs. 2 and 3, there is seen to be little to choose between the two catalysts.

Summary

1. The decomposition of ethylene glycol in the presence of vanadium pentoxide has been studied.
2. Acetaldehyde and ethylene are the principal products.
3. Curves showing the relative amounts of the individual products formed are given.

College Park, Maryland