

$D_{(C-H)}$ in ethylene since the value of 122 kcal. gives $E_1 = 39 \pm 2$ kcal., which seems unduly large.

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[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

The Thermal Decomposition of Mono-2-ethylhexyl Polypropylene Glycol

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The thermal decomposition reactions of mono-2-ethylhexylpolypropylene glycol were studied. The decomposition is free radical in nature and is catalyzed by oxygen or peroxides. The behavior of the free radical polymer molecule is controlled by the ease with which ether bonds are broken in the formation of carbonyl groups. This effect also controls the production of volatile products arising from radical fragments of the original molecules.

The polypropylene glycols comprise a class of synthetic polymeric materials possessing many interesting physical properties. Their chemical behavior is informative because their structure offers unique opportunity for studying the ether linkage. This paper reports a study of the thermal decomposition of a mono-2-ethylhexylpolypropylene glycol having an average molecular weight of about 1000.

Experimental

Materials.—The polypropylene glycol was prepared by polymerization of propylene oxide. The reaction was initiated with 2-ethylhexanol and catalyzed by sodium 2-ethylhexanolate. This material was purified and topped in the usual manner yielding number average molecular weights of 1000 and 920, determined by end group analysis and freezing point lowering, respectively. The polymer viscosity at 100° was 11.4 centistokes. To ensure that the results obtained with this material were typical of the class of compounds, several critical measurements were repeated with a sample of polypropylene glycol P-1200 obtained from the Dow Chemical Company. No significant differences were noted.

Thermal Decomposition Measurements.—The rate of thermal decomposition was determined by measuring the rate of increase of pressure in a closed system due to the formation of highly volatile products. A weighed amount of the material (10 g. in all cases) was introduced into the reaction tube, which was heated by a vapor bath, and the gas handling system was filled to a pressure of 20 mm. with oxygen-free N_2 . The system was designed so that all of the lower molecular weight products, except those highly volatile, were maintained in the tube by reflux. Measurements were started at a given time after the reflux level of the vapor bath reached a fixed position. The temperature of the bath was determined separately with a mercury thermometer, and the pressure was determined with a mercury manometer. By closing appropriate stopcocks, gas samples for analysis were obtained in a sample bulb contained in the gas handling system.

Catalytic Effect of Oxygen.—Determination of the catalytic effect of oxygen was carried out in apparatus very similar to that described above, except that the reaction tube was equipped with an inlet line at the bottom so that gas pumped by a Sigmamotor pump could be circulated through the system. The gas, composed of nitrogen and oxygen in predetermined proportions, was initially near atmospheric pressure. The reaction was followed by observing the change in pressure.

Catalytic Effect of Peroxides.—The catalytic effect of peroxide upon the thermal decomposition reaction was determined by decomposing a given quantity of di-*t*-butyl peroxide in the polyglycol and then stripping off the peroxide decomposition products plus any low molecular weight

polyglycol fragments produced by reaction of free radicals derived from the peroxide. The weight loss of polymer and the viscosity change of the residual material were determined. The residual material was examined by infrared analysis to determine the principal functional groups produced.

Analyses.—Gas analysis for all components, with the exception of formaldehyde, was carried out using infrared and mass spectrometry. Acetaldehyde, propylene, carbon monoxide and acetone were identified and determined quantitatively using a Perkin-Elmer Model 21, dual beam, infrared spectrometer.¹ These values were confirmed by mass spectrometric analyses and determination made of propionaldehyde. Formaldehyde was determined polarographically² in an aqueous solution obtained by extracting the sample bulb with water. In the experiments designed for the determination of formaldehyde, the apparatus was heated to ensure that all condensation took place in the sample bulb. The presence of formaldehyde was confirmed by ultraviolet and infrared analysis in experiments wherein the gaseous products were fed into heated cells which prevented condensation from occurring.

Carbonyl determinations on the residual liquid samples were made by a modification of the method of Stillman and Reed.³ Hydroxyl determinations were made using acetyl chloride and pyridine, while unsaturation was determined by the method of DuBois and Skoog.⁴

Molecular weights of degraded samples were determined by a freezing point lowering method.

Results

Thermal Decomposition.—The decomposition rates of the polypropylene glycol at two temperatures are shown in Fig. 1, where the volume of gaseous decomposition products measured in cubic centimeters at normal temperature and pressure per 10 g. of oil is plotted against time in minutes. Detailed analyses of the gaseous products from a number of runs at 338° were made, the average result of which are given in Table I. The average sample was collected after 7.5 minutes. The actual pressure of gaseous products in the system at this point was 80 mm. This low sample collection pressure was used to avoid condensation. The average results of analyses of the liquid residues remaining after formation of the gas sample discussed above are also given in Table I.

(1) J. T. Neu, *J. Opt. Soc.*, **43**, 520 (1953).

(2) G. C. Whitnack and R. W. Moshier, *Ind. Eng. Chem., Anal. Ed.*, **16**, 496 (1944).

(3) A. C. Stillman and R. M. Reed, *Perfumery Essential Oil Record*, **23**, 228 (1932).

(4) H. D. DuBois and D. A. Skoog, *Anal. Chem.*, **20**, 624 (1948).

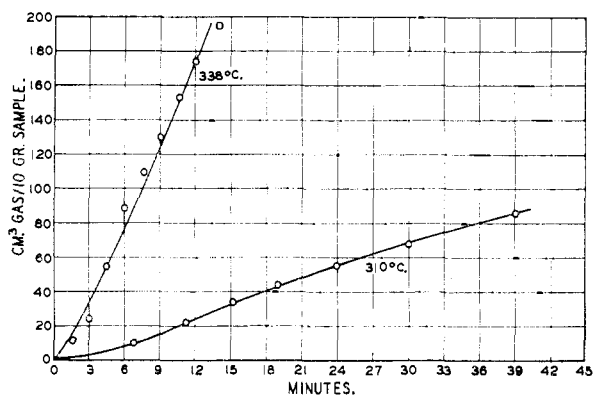


Fig. 1.—Rate of thermal decomposition of polypropylene glycol as measured by production of volatile products.

TABLE I

ANALYTICAL DATA OF THERMAL DECOMPOSITION PRODUCTS AT 338° FROM 10 G. (10.8×10^{-3} MOLE) OF MONO-2-ETHYLHEXYLPOLYPROPYLENE GLYCOL

Gaseous products (moles $\times 10^3$)		Residual oil products (moles $\times 10^3$)	
CH ₃ CHO	1.6	Carbonyl	3.9
H ₂ CO	1.2	Hydroxyl	0.2
CH ₃ CH ₂ CHO	0.6	Unsaturation	0.2
CH ₂ =CHCH ₃	0.5	Viscosity at 100° cs.	8.8
CO	0.3	Mol. wt.	700
CH ₃ COCH ₃	0.1		
Unaccounted for, 4% of total			

To ensure that no major differences would result in the gaseous product distribution at longer times, several runs were made in which the reaction was carried to the point described above, the reaction vessel cooled to room temperature, evacuated, brought to temperature, and the products determined again. No differences were found.

Attempts were made to inhibit the thermal decomposition at 338° with N-phenyl-1-naphthylamine, a good oxidation inhibitor possessing a labile hydrogen atom, without success even at concentrations as high as 5%.

No extensive work was done at temperatures other than 338°. Survey experiments showed that at temperatures as low as 260° acetaldehyde, carbon monoxide, acetone and propylene were still among the decomposition products, although their ratios were somewhat changed from those at higher temperatures.

Oxygen Catalysis.—When the decomposition was carried out at lower temperatures with oxygen catalyst, the change of pressure as a function of time was obtained. In these experiments, which were carried out at temperatures low enough so that the strictly thermal rates of decomposition were zero as measured under these conditions, the point of interest is the magnitude of the pressure increase following completion of reaction, as determined by the cessation of a pressure change. At this point, essentially all of the oxygen had been absorbed, as shown by mass spectroscopic analysis. Analytical data resulting from one experiment at 241° where oxygen at 40 mm. had been absorbed (corresponding to a ratio of moles of oxygen adsorbed to moles of polymer of 0.2) and products

formed corresponding to a pressure of 62 mm. is given in Table II.

TABLE II

ANALYSIS OF GASEOUS PRODUCTS RESULTING FROM OXYGEN-CATALYZED DECOMPOSITION OF MONO-2-ETHYLHEXYLPOLYPROPYLENE GLYCOL AT 241°

Gaseous products (moles $\times 10^3$)		Residual oil	
Acetaldehyde	1.8	Mol. wt.	800
Acetone	0.3	Viscosity at 100°, cs.	8.9
Carbon monoxide	0.3		
Propylene	0		

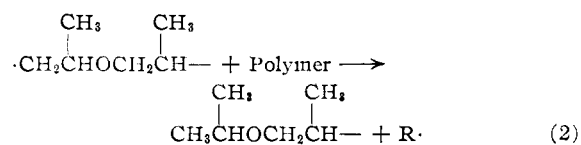
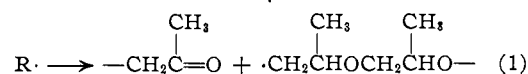
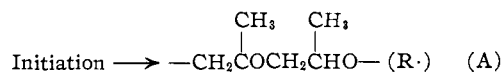
Peroxide Catalysis.—When di-*t*-butyl peroxide was thermally decomposed in polypropylene glycol, the viscosity of the residual oil (after stripping off the low boiling peroxide decomposition products) decreased, and a fraction of the initial oil was converted to low molecular weight products which were removed in stripping. For example, when 84 mmoles of di-*t*-butyl peroxide was decomposed at 115° in 108 mmoles of polyglycol (100 g.), 4.5 g. of the material was converted to low boiling products. The viscosity of the residual oil at 100° decreased from 11.4 to 9.2 cs. Infrared analysis showed this residual phase to have a high carbonyl content.

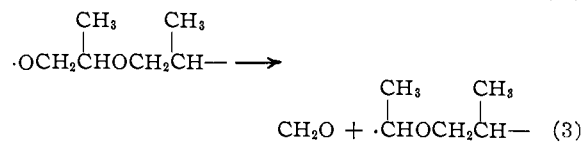
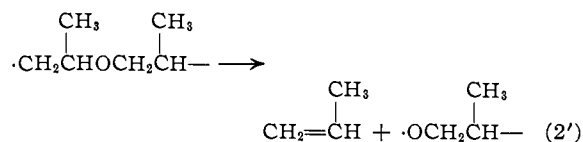
Discussion

An important fact to establish in discussing the mechanism of a thermal decomposition reaction is to determine whether it is primarily a free radical reaction or an intramolecular rearrangement. The array of decomposition products obtained from the polyglycol, which appears to be most easily accounted for by free radical mechanisms, and the catalytic effect of oxygen and peroxide in inducing decomposition demonstrates that the decomposition reaction is primarily of a free radical nature.

The large decrease in molecular weight of the residual oil as a result of thermal decomposition, amounting to 14% for a 1% decomposition of the polymer into volatile products, suggests that the reaction proceeds *via* random chain scission. The production of carbonyl groups resulting from free radical induced chain scission (*t*-butyl peroxide experiments), as well as in the strictly thermal reaction, suggests that the principal factor controlling polyglycol behavior arises from the instability of the radical formed by loss of a hydrogen atom adjacent to an ether link.

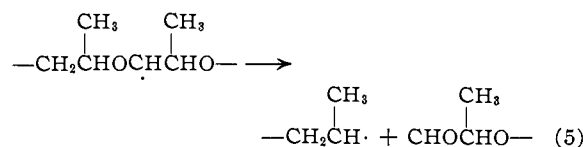
Considering this effect to be of primary importance, the following mechanism for the thermal decomposition of polypropylene glycols satisfactorily accounts for the experimental observations



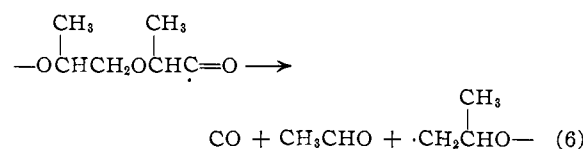


Because in reactions (3) and (4) no more formaldehyde and acetaldehyde can be formed than corresponds to the propylene formed in reaction (2'), 0.7×10^{-3} and 1.1×10^{-3} mole of formaldehyde and acetaldehyde, respectively, must have been formed in another manner. Reaction of the alkoxy radical, formed in reaction (2') with polymer to form an alcohol would reduce the yield of light aldehydes; however, in view of the small amount of hydroxyl formed (0.2×10^{-3} mole), this apparently does not occur often. Similarly, it is assumed that the reaction of the radical formed in reaction (3) with polymer is slow compared with reaction (4).

If, in reaction (2), a secondary radical was formed rather than the tertiary radical shown, the resulting product would be an aldehyde rather than a ketone; *i.e.*



Reactions of fragment radicals would be similar to those in (2'), (3) and (4) and would yield the same products. Abstraction of the labile hydrogen association with the aldehyde group gives rise to carbon monoxide and acetaldehyde, as in reaction (6)

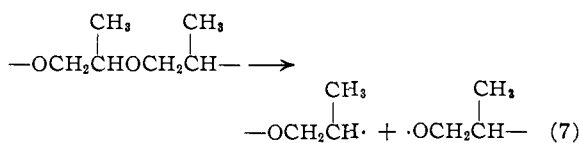


Assuming that an amount of acetaldehyde equivalent to the carbon monoxide is produced in reaction (6) leaves 0.8×10^{-3} mole of acetaldehyde unaccounted for, as well as 0.7×10^{-3} mole of formaldehyde previously discussed.

The lack of inhibitory action of N-phenyl-1-naphthylamine suggests that the chain length of the primary chain reaction is small and that the material produced in the initiation reaction is of importance. This belief is substantiated by the experiment previously described, in which oxygen was used as a catalyst at 241° . In this case the ratio of the number of moles of chain scission per mole of

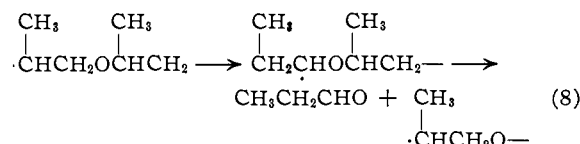
oxygen absorbed, determined from the decrease in molecular weight, is close to unity.

The most likely initiation reaction is that given in reaction (7), or the corresponding dissociation of a carbon-carbon bond if both bonds have similar dissociation energies



If the residual formaldehyde and acetaldehyde are produced from the resulting radicals, as in reactions (3) and (4), and if chain termination results primarily from radical recombination, the chain length is calculable and is equal to 5.5. That chain termination probably results primarily by radical recombination rather than by disproportionation is indicated by the small amount of unsaturation observed in the residual oil (Table I).

Accounting for the propionaldehyde and acetone formed in a uniquely satisfactory manner is difficult. It is proposed that they are formed by isomerization of propyl radical end groups, as shown in reaction (8) for the production of propionaldehyde.



Based upon the above scheme of decomposition, the expected molecular weight of the residual oil can be calculated, because essentially all of the molecular scissions give rise to carbonyl groups in the residual oil. Using the figures given in Table I, an expected molecular weight of 660 is obtained, compared with an observed value of 700.

While the experimental data are not extensive enough to obtain firm activation energies, it is informative to calculate an activation energy for the initiation reaction (7) utilizing the information available. Using a rate of initiation obtained from the amounts of acetaldehyde and formaldehyde produced in reaction (7) and assuming a frequency factor of 10^{14} sec.⁻¹, an activation energy of about 55 kcal./mole for the dissociation energy of the C-O bond, estimated by Rebbert and Laidler,⁵ and 80.0 kcal./mole for the normal C-C bond, this low value indicates an effect of the polyether structure upon these dissociation energies.

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(5) R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, **20**, 574 (1952).