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

The Polymeric Peroxide of Methacrylonitrile[1]

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The relatively stable polymeric peroxide of methacrylonitrile, having a maximum content of 26.7% by weight of peroxide oxygen (the theoretical 1:1 copolymer contains 32.3%), was prepared by the action of oxygen on the monomer, with or without added initiator. The peroxide could be analyzed iodometrically, and the resulting values for peroxide content showed excellent correlation with the quantitative yields of carbonyl compounds obtained in thermal decompositions. The peroxide was reduced smoothly with zinc and acetic acid to yield the cyanohydrin of hydroxyacetone. Decomposition reactions in alcohols and other solvents showed that pyruvonitrile and formaldehyde were the predominant primary decomposition products, but varying amounts of reductive cleavage products were also obtained.

Polymeric peroxides have been obtained from diphenyl ethylene,[2a] α-terpinene,[2b] styrene,[2c] indene,[2d] chloroprene,[2e] methyl methacrylate,[2f] vinyl acetate,[2f] 2,3-dimethylbutadiene,[2g] acrylonitrile[2h] and α-methylstyrene.[2i] The polymeric peroxide of styrene has been studied[3] in considerable detail.

Although many polymeric peroxides have been reported, their reactions have generally not been studied thoroughly. It seemed of interest to learn the effect of the cyano group on the properties of a polymeric peroxide. Knowledge of the behavior of nitrile-containing polymeric peroxides was also desired in order to interpret the results of the reaction of oxygen with acrylonitrile and methacrylonitrile in aqueous systems.[2h,4] Since earlier work showed that acrylonitrile yielded only a highly unstable peroxide, methacrylonitrile was chosen for further studies. The formula of the ideal 1:1 copolymer of oxygen and methacrylonitrile would be

$$[-OCH_2C(CH_3)(CN)O-]_n$$

Discussion

The polymeric peroxide of methacrylonitrile was prepared by passing a stream of oxygen through a well-stirred mass of monomer at a temperature of 45–50°. Ultraviolet light increased the yield, although the product contained less peroxidic oxygen than did the one prepared in the dark. The use of α,α'-azodiisobutyronitrile as an initiator yielded a product which was similar to the one obtained in the absence of the initiator, while diacetyl with ultraviolet light yielded a product having low molecular weight and low peroxide content. In Table I are shown the results of several preparations of peroxide, along with some of the characteristic properties.

TABLE I

COMPARISON OF PEROXIDE PREPARATIONS

Type of initiation	Reaction time, hr.	Yield, %	Peroxide[e] O_2, % by wt.	Mol. wt.	Explosive dec temp., °C.
Diacetyl + ultraviolet	29.5	14.8	15.8	810[b]	140–150
Ultraviolet	16.5	14.8	20.2	...	..
Ultraviolet	68	21.3	21.3	1400[c]	162
Ultraviolet	74	26.3	21.0	1760[c]	..
AIBN[a]	37.5	6.9	26.6	High[d]	..
None	48	2.7	26.7	High[d]	165
None	120	10.2	26.7	High[d]	..

[a] α,α'-Azodiisobutyronitrile. [b] Obtained by freezing point depression in benzene. [c] Obtained by freezing point depression in ethylene bromide. [d] These samples were not soluble in ethylene bromide. [e] Theoretical value for a 1:1 copolymer with oxygen is 32.3%.

From the data of Table I it is evident that increased reaction time resulted in an increased yield of polymeric peroxide, although the peroxide content was not affected appreciably. The limiting value of peroxide oxygen, regardless of type of initiation, was 27% by weight.

When the reaction was run in the dark, normal polymerization, *i.e.*, formation of oxygen-free polymethacrylonitrile, was completely inhibited. However, in the presence of ultraviolet radiation, a small amount of polymethacrylonitrile was produced. This is probably due to the higher rate of initiation, since the polymeric peroxide itself is capable of initiating polymerization in ultraviolet light.

Other products accompanying the polymeric peroxide were formaldehyde, pyruvonitrile, carbon dioxide and carbon monoxide. During one preparation in ultraviolet light, quantitative determinations of gaseous products showed that the molar quantity of formaldehyde was at least three times as great as that of the carbon dioxide. It is likely that the carbon monoxide and carbon dioxide result from the oxidation of formaldehyde, a reaction which would be enhanced by ultraviolet radiation. When the reaction was carried out in the dark, very little carbon dioxide was produced.

Probably some of the formaldehyde and pyruvonitrile resulted from the decomposition of polymeric peroxide, especially in the presence of ultraviolet light, which accelerates the decomposition. However, in the reaction of oxygen with styrene in the absence of ultraviolet light, Miller[3b] found that the formation of formaldehyde and benzaldehyde did not result directly from the polymeric peroxide or from a bimolecular reaction of styrene with oxygen. The exact mechanism of formation remains in doubt.

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[1] From the Ph.D. Thesis of Sterling F. Strause, 1955. Supported by research grant NSF-G578 of the National Science Foundation.

[2] (a) H. Staudinger, *Ber.*, **58**, 1075 (1925); (b) E. H. Farmer, *I.R.I. Transactions*, **21**, No. 2 (1946); (c) F. A. Bovey and I. M. Kolthoff, THIS JOURNAL, **69**, 2143 (1947); (d) V. Gutmann, *J. Polymer Sci.*, **3**, 336, 518, 642 (1948); (e) W. Kern, H. Jockusch and A. Wolfram, *Makromol. Chem.*, **3**, 223 (1949); (f) C. E. Barnes, R. M. Elofson and G. D. Jones, THIS JOURNAL, **72**, 210 (1950); (g) W. Kern and J. Stallmann, *Makromol. Chem.*, **7**, 199 (1951); (h) K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952); (i) G. A. Russell, *ibid.*, **75**, 5011 (1953).

[3] (a) F. R. Mayo, Abstracts of the A.C.S. Meeting, Chicago, Sept. 1953, p. 35-O; (b) A. A. Miller, THIS JOURNAL, p. 35-O.

[4] E. Dyer, O. A. Pickett, Jr., S. F. Strause and H. E. Worrell, *ibid.*, in press.

No cyanogen[5] or hydrogen cyanide was detected during the reaction in the presence of ultraviolet light. This indicates that the cyano group was not labilized during the reaction.

It was found that the method of peroxide analysis reported by Barnes and co-workers,[2f] which utilized hydriodic acid in acetic acid at 100°, was not satisfactory for the polymeric peroxide of methacrylonitrile. Control experiments[6] showed that the amount of iodine liberated varied with the time of heating. The method of Nozaki,[7] using sodium iodide and acetic anhydride, gave values for peroxide content which were reasonably accurate and precise. Additional justification of the accuracy of this method of analysis comes from quantitative data on thermal degradation, discussed in a later section.

The data on peroxide content of the polymers, given in Table I, show that even under optimum conditions the copolymer contained 1.3 parts of methacrylonitrile for one part of oxygen. Experimental evidence indicates that the polymeric peroxide does contain segments of several monomer units.

The peroxide linkages in this polymer were evidently more easily reduced by iodide than the linkages in the polymeric peroxides of styrene, α-methylstyrene and indene, since Russell[21] stated that conventional methods failed with those peroxides.

When a small amount of polymeric peroxide was suddenly heated above 165°, it decomposed with an audible explosion. The explosive decomposition temperature, as shown in Table I, does not vary appreciably with molecular weight.

The main products of thermal decomposition of the polymeric peroxide were formaldehyde and pyruvonitrile, but small amounts of pyruvaldehyde and hydroxyacetone were also produced. This indicates that some reductive cleavage took place by abstraction of hydrogen atoms from decomposition products or from peroxide molecules.

Quantitative thermal decomposition, accomplished by dropping a chloroform solution of the peroxide on a glass surface at 300° in an atmosphere of nitrogen showed that at least 92% of the decomposition occurred by chain scission to formaldehyde and pyruvonitrile. These experiments prove that the major portion of the peroxide consisted of a 1:1 copolymer of methacrylonitrile and oxygen. Typical data may be interpreted in two ways to support the accuracy of the peroxide determinations which were obtained iodometrically. Assuming that every peroxide linkage produced one molecule of formaldehyde or one of hydroxyacetone, duplicate decomposition experiments showed 21.7 and 20.3% (average 21.0%) by weight of peroxidic oxygen, while iodometric analysis showed 21.3%. The value of 21.0% by weight of peroxidic oxygen corresponds to 65% of the theoretical oxygen content based on a 1:1 copolymer. If the value for peroxide content from iodometric analysis is used to calculate the expected yields of carbonyl compounds from thermal decomposition, then the yields of products are 101.6 and 95.1% of theoretical (average 98.4%).

The polymeric peroxide of methacrylonitrile was readily reduced to the cyanohydrin of hydroxyacetone by a large excess of zinc dust in glacial acetic acid. This serves as further proof of the copolymer structure of the peroxide. The reaction was exothermic, and only trace quantities of formaldehyde and pyruvaldehyde were produced.

The ease of reduction may be characteristic of polymeric peroxides. Russell[21] found that hydroperoxides and polymeric peroxides were far more reactive toward lithium aluminum hydride than were most dialkyl peroxides.

Bulk polymerization experiments with the polymeric peroxide as an initiator showed that it decomposes by a free radical mechanism, which is greatly accelerated by ultraviolet light.

Solutions of the polymeric peroxide in various solvents were subjected to elevated temperatures to determine the mode of decomposition. From the formula of a 1:1 copolymer of oxygen and methacrylonitrile, given earlier, it may be seen that scission of the peroxide linkage followed by cleavage of the adjacent carbon to carbon bond would yield formaldehyde and pyruvonitrile. When active hydrogen atoms are available, reductive cleavage would result in the formation of hydroxyacetone cyanohydrin, and any liberated hydroxyacetone could be oxidized to pyruvaldehyde. The results of the quantitative determination of decomposition products are shown in Table II.

TABLE II

DECOMPOSITION OF PEROXIDE IN SOLVENTS

Solvent	Temp., °C.	Time, hr.	HCHO, % yield	Acetol,[b] % yield
$CHCl_3$[a]	55	35	18.5	None
$BrCH_2CH_2Br$[a]	75	35	33.4	None
$BrCH_2CH_2Br$[a]	130	2	29.7	11.5
CH_3COOH	100	24	60.1	4.5
CH_3OH	65	7	17.7	15.5
CH_3OH	65	16	28.2	14.8

[a] The peroxide was not completely decomposed at the end of the reaction. [b] Values in this column represent the sum of hydroxyacetone and pyruvaldehyde.

The yields are not as high as might be expected, but it must be realized that other products may be forming in small amounts and that some of the cyanohydrins may escape detection. Nevertheless, definite trends are obvious. Chloroform at 55°, ethylene bromide at 75°, and glacial acetic acid at 100° appear to comprise a series in which the rate of decomposition is a function of temperature. Apparently the reaction is primarily chain cleavage to produce formaldehyde. It is quite likely that these decompositions proceed by a free radical mechanism.

A comparison of the data at 75 and 130° in ethylene bromide shows that the time required for the same extent of decomposition was very different. This change was corroborated by visual observation of the thermal decomposition of peroxide in the absence of solvent, when a marked change in rate of decomposition occurred as the temperature

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[5] Test made by the methods of L. M. Dennis, "Gas Analysis," The Macmillan Co., New York, N. Y., 1913, p. 265.

[6] Acknowledgment is made to Dr. F. R. Mayo for helpful discussion on this subject.

[7] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

reached 90–100°. In ethylene bromide the change to higher temperature apparently favored acquisition of hydrogen atoms from the solvent, since an appreciable amount of reductive cleavage product was obtained at 130°.

The rate of decomposition was much greater in methanol than in other solvents used. In this case some of the formaldehyde resulted from the oxidation of methanol.

Decomposition of the polymeric peroxide in a series of alcohols showed that the predominant products were hydrogen cyanide, formaldehyde, the acetate of the alcohol, and an oxidation product which resulted from the alcohol. This latter product was formaldehyde, acetaldehyde or acetone in the case of methyl, ethyl or isopropyl alcohols, respectively. Relatively small amounts of pyruvaldehyde and the cyanohydrin of hydroxyacetone were found.

The experiments which have been performed with alcohols do not allow a rigorous establishment of the mechanism of reaction. However, the results of product studies are consistent with a mechanism which involves the predominant formation of formaldehyde and pyruvonitrile. The latter compound reacts readily with methanol to yield hydrogen cyanide and methyl acetate. Alternative acquisition of hydrogen atoms by free radicals resulting from homolytic cleavage of peroxide links would account for the production of hydroxyacetone cyanohydrin and related compounds. Attack of the alcohol by free radicals involved in the decomposition would result in the oxidation of the alcohol.

When the peroxide was decomposed in methanol in the presence of hydroquinone, no more than a trace of quinhydrone or quinone was found. This indicates that the peroxide, while assuming the role of an oxidizing agent, preferentially attacked the alcohol.

There is a striking difference in thermal stability of the polymeric peroxides of methacrylonitrile and acrylonitrile,[2h] and apparently the added methyl group in the former is the chief factor contributing to the increased stability. Similar effects have been noticed with methyl vinyl ketone and methyl isopropenyl ketone.[8] While this effect is not yet completely understood, it may be linked to the generally increased stability of tertiary peroxides, since the presence of the added methyl substituent results in a peroxide having a tertiary carbon atom on one side of the peroxide linkage.

Experimental

Methacrylonitrile.[9]—The monomer was washed with saturated sodium bisulfite solution, 1% sodium hydroxide and water. After drying over calcium chloride, the material was fractionated through a Widmer column to remove final traces of methacrolein and acetone; b.p. 90.2°, $n^{20}\text{D}$ 1.4006[10]; negative test for carbonyl compounds.

Solvents.—All solvents were dried and distilled. In addition, isopropyl alcohol was refluxed with stannous chloride to remove peroxides, and petroleum ether was freed from olefins.

Hydroxyacetone Cyanohydrin.—To a solution of 0.097 mole of the bisulfite addition product of hydroxyacetone[11] in 45 ml. of water at 16° was added dropwise a solution of 0.1 mole of potassium cyanide in 11 ml. of water, maintaining the temperature at 15–20°. The resulting mixture was acidified to a *p*H of 3 with dilute sulfuric acid at 15–20°. After continuous ether extraction, drying of the extract, and distillation under reduced pressure, the cyanohydrin was obtained, b.p. 130° at 19 mm., $n^{20}\text{D}$ 1.4391; yield approximately 20%.

Hydroxyacetone Benzoate.—Treatment of hydroxyacetone cyanohydrin with excess benzoyl chloride in pyridine yielded only hydroxyacetone benzoate, b.p. 101–102° at 2 mm. Its 2,4-dinitrophenylhydrazone melted at 189–190.3° after several recrystallizations from ethyl acetate. The reported[12] melting point is 184–186°.

Identification Procedures. 2,4-Dinitrophenylhydrazone of Formaldehyde.—Chromotropic acid was found to react with the 2,4-dinitrophenylhydrazone of formaldehyde by heating in concentrated sulfuric acid, giving the violet color which is characteristic of formaldehyde.[13] Under the same conditions the following compounds did not interfere: acetaldehyde, acetone, pyruvic acid, pyruvonitrile, pyruvamide, diacetyl, pyruvaldehyde and glyoxal.

Pyruvonitrile.—Reactions used for the identification of pyruvonitrile[14] include (a) the reaction with water[15] to give acetic acid and hydrogen cyanide and (b) the formation of pyruvamide and/or pyruvic acid by treating with concentrated hydrochloric acid at 0° and then boiling the solution for one minute. The pyruvamide and pyruvic acid form 2,4-dinitrophenylhydrazones, melting at 217.5–219° and 214–215.5°, respectively, which are separable with sodium carbonate.[16]

Hydroxyacetone.—Specific color tests are the reactions with *o*-aminobenzaldehyde[17] and with *o*-nitrobenzaldehyde.[18] Pyruvic aldehyde is negative in both tests, but pyruvic acid responds to the second. A convenient derivative of hydroxyacetone is the 2,4-dinitrophenylhydrazone of the benzoate.[12]

Pyruvaldehyde.—As a specific test the green fluorescence with chromotropic acid[19] in sulfuric acid was used. Hydroxyacetone does not interfere.

Preparation of Polymeric Peroxide.—A stream of dry, carbon dioxide-free oxygen was introduced through a gas-dispersing tube into 125 ml. of methacrylonitrile, agitated by a magnetic stirrer, in a Pyrex flask kept at 45–50°. The exit gases were passed through a Graham type reflux condenser into various test solutions. The source of ultraviolet light was a General Electric sunlamp. The polymeric peroxide separated as an oily layer upon the addition to the reaction mixture of at least two volumes of petroleum ether, a solvent for the monomer and pyruvonitrile. The peroxide layer was evacuated at room temperature until volatile materials were removed. The residual, very viscous, tacky product was stored in a stoppered container at 0°. Small amounts of polymethacrylonitrile could be removed by dissolving the viscous mass in an appropriate solvent and reprecipitating the peroxy polymer with petroleum ether.

Anal. Calcd. for $C_4H_5NO_2$: C, 48.48; H, 5.09; N, 14.14; peroxide O, 32.3. Found: C, 49.13; H, 5.80; N, 12.98; peroxide O, 21.3.

Normal polymer was formed along with peroxy polymer in the presence of ultraviolet light. In certain preparations, when stirring was inadequate, as much as 14% of the product was insoluble in ethylene bromide. When efficient stirring was used, the product, though completely soluble in ethylene bromide, left a normal polymer residue of 6% when the peroxy polymer was decomposed in methanol. It is possible that the polymethacrylonitrile was originally present as segments of chains containing peroxy linkages.

Hydroperoxides were absent, as shown by negative results when the Criegée test[20] for allylic hydroperoxides was

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[8] O. A. Pickett, Jr., Ph.D. Thesis, University of Delaware, 1955.

[9] Kindly furnished by the Shell Development Company.

[10] Shell Development Company, Report No. S-9976 (1947).

[11] P. A. Levene and A. Walti, *Org. Syntheses*, **10**, 1 (1930).

[12] R. Adams and T. R. Govindachari, THIS JOURNAL, **72**, 162 (1950).

[13] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

[14] Prepared by the method of W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

[15] F. C. Whitmore, "Organic Chemistry," Sec. Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 365.

[16] E. Simon and C. Neuberg, *Biochem. Z.*, **232**, 479 (1931).

[17] O. Baudisch and H. J. Deuel, THIS JOURNAL, **44**, 1585 (1922); E. Werle and P. Stiess, *Biochem. Z.*, **321**, 485 (1951).

[18] O. Baudisch, *ibid.*, **89**, 279 (1918).

[19] B. J. Thornton and J. C. Speck, *Anal. Chem.*, **22**, 899 (1950).

[20] R. Criegée, H. Pilz and H. Flygare, *Ber.*, **72**, 1799 (1939).

applied to various samples of the peroxide, as well as to residual materials from the decanted petroleum ether solutions obtained during isolation of the peroxide. Also, the infrared spectra of the peroxy polymers showed no absorption at 12–12.5 μ, a region of absorption characteristic of many alkyl hydroperoxides.[21]

Pyruvonitrile was isolated from the petroleum ether solution by flash distillation at room temperature under reduced pressure, followed by fractionation of the distillate.

The exit gases from preparation of the peroxy polymer contained carbon dioxide, carbon monoxide and formaldehyde, identified as previously described.[2h]

Properties of the Polymeric Peroxide.—All samples of the polymeric peroxide were soluble in chloroform, methanol, ethyl acetate, acetone, acetic acid and acetic anhydride, and insoluble in carbon tetrachloride and saturated aliphatic hydrocarbons. Only the low molecular weight material was soluble in benzene, and all except the samples prepared in the dark were soluble in ethylene bromide. Peroxide having a molecular weight of 1760 was entirely miscible with methanol but only slightly soluble in ethanol and isopropyl alcohol.

The infrared absorption spectrum of the polymeric peroxide showed a nitrile band at 4.5 μ, weak bands at 5.8 and 6.2 μ, due to carbonyl and double bonds (possibly due to adhering decomposition products), strong absorption at 8.2, 8.9, 9.6 and 10.7 μ and a weak band at 11.8 μ. Some of the bands in the 8–11 μ region are close to those reported by Karyakin and Nikitin[22] for several peroxides. In general the spectrum is rather similar to the one reported for the polymeric peroxide of acrylonitrile.[2h]

The ultraviolet absorption spectrum determined with a 1% solution in chloroform showed that while complete transmission occurred at 400 mμ, absorption increased with decreasing wave length, and only 2% of the incident light was transmitted at 260 mμ.

Peroxide Analysis.[23]—A sample of peroxide was dissolved in acetic anhydride. An aliquot portion containing about 0.05 g. of peroxide was treated as in the Nozaki method,[7] allowing a 20-minute period of standing with the iodide before titration with 0.02 *N* sodium thiosulfate. Control tests showed that prolonging the reaction time from 20 to as long as 120 minutes increased the peroxide value by only 5 parts per 1000. More than 99% of the iodine was liberated after only 10 minutes. Analyses of four different aliquot portions of a polymer sample containing 21.2% by weight of peroxidic oxygen gave a standard deviation of 0.0336 and a variance of 0.00113.

In the analysis of peroxides prepared in the dark, minute particles of solid white material appeared after titration of the iodine. This material apparently resulted from the liberation of segments of several monomer units which were present in the peroxy polymer chains.

Initiation of Polymerization.—Used in a concentration of 0.2% by weight, the polymeric peroxide gave a 31% conversion of pure acrylonitrile to polymer in 2 hours at 30–35° in the presence of ultraviolet light, whereas a conversion of only 1.3% resulted at 50° without ultraviolet light after 25 hours. The same concentration of polymeric peroxide in styrene at 80° gave a 42% conversion in 30 hours, while a blank showed 17% conversion.

Thermal Decomposition of Peroxide.—When a 3-g. sample of the polymeric peroxide was heated at 0.25 mm. pressure, decomposition started at 75° and became vigorous at 85–110°. The products, collected in traps cooled to −11° and to −80°, consisted of formaldehyde, pyruvonitrile, pyruvaldehyde and hydroxyacetone.

Flash decomposition[6] at atmospheric pressure was used when quantitative data on products were desired. A solution of 0.4 g. of the peroxide in chloroform was admitted dropwise to a 100-ml. flask heated to 300° by a mantle and arranged for passage of exit gases through cold traps and wash bottles containing aqueous 2,4-dinitrophenylhydrazine hydrochloride. Nitrogen was passed through the system continuously. The 2,4-dinitrophenylhydrazones collected from all traps were filtered through weighed crucibles. The formaldehyde derivative could be separated quantitatively from the pyruvaldehyde 2,4-dinitrophenylhydrazone by the solubility of the former in boiling 94% ethanol.[24] Separate tests showed a considerable amount of pyruvonitrile in the first cold trap, but it was not determined quantitatively.

Reduction of Polymeric Peroxide.—A solution of 1.5 g. of peroxide in 70 ml. of glacial acetic acid was treated with 71 g. of zinc dust added in portions at a rate sufficient to keep the temperature at 44–47°. After stirring at room temperature for 7 hours, the filtrate was diluted to 100 ml. with acetic acid, and aliquot portions were used for quantitative determination of carbonyl compounds with 2,4-dinitrophenylhydrazine. Only traces of the formaldehyde derivative were obtained, while 23 and 26% yields of the 2,4-dinitrophenylosazone of hydroxyacetone (or pyruvaldehyde) were obtained in duplicate experiments. Tests on separate portions of the reduction mixture proved the presence of appreciable amounts of the cyanohydrin of hydroxyacetone. Small amounts of pyruvaldehyde were also detected.

Decomposition in Solvents at Elevated Temperatures.—The peroxide used for these experiments had been prepared in the presence of ultraviolet light. In general, a solution of approximately 0.35 g. of peroxide in 25 ml. of solvent was placed in a 50-ml. flask equipped with reflux condenser and heated in a bath. A stream of nitrogen was passed through the system and into an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride to trap formaldehyde as the 2,4-dinitrophenylhydrazone. At completion of the reaction an aqueous solution of the water-soluble decomposition products was heated on the steam-bath under reflux for seven hours with excess 2,4-dinitrophenylhydrazine hydrochloride. All 2,4-dinitrophenylhydrazones were collected, and the derivatives of formaldehyde and pyruvaldehyde were separated by means of hot 94% ethanol.

Decomposition in Alcohols.—For the purpose of determining the products of the reaction of polymeric peroxide with methyl, ethyl and isopropyl alcohols, 3.5 g. of peroxide in 150 ml. of alcohol was heated under reflux with stirring for 18 hours. Nitrogen was swept through the system and the gaseous products were trapped as before. With ethyl and isopropyl alcohols, the reaction mixture was heterogeneous initially. At completion of the reaction no appreciable amount of peroxide remained. The solution was flash distilled under reduced pressure at room temperature, leaving a residual liquid, and the distillate was carefully fractionated by means of a Widmer column. Thorough investigation showed the presence of the compounds shown in Table III.

TABLE III

PRODUCTS OF DECOMPOSITION OF POLYMERIC PEROXIDE IN ALCOHOLS

CH_3OH	C_2H_5OH	i-C_3H_7OH
HCN[a]	HCN[a]	HCN[a]
HCHO	HCHO	HCHO
CH_3COOCH_3[b,c]	$CH_3COOC_2H_5$[b,c]	Ester[c]
....	CH_3CHO[d]	CH_3COCH_3[d]
$CH_3C(OH)(CN)CH_2OH$[e]	CH_3COCH_2OH	CH_3COCHO

[a] Detected in the gas stream and in the reaction mixture. [b] Identified by b.p. of the azeotrope (with the alcohol) and by the preparation of *p*-methylacetanilide,[25] m.p. 145–147.5°, which did not lower the m.p. of an authentic sample. [c] Positive hydroxamic acid test for an ester.[26] [d] Identified in the gas stream and the flash distillate as the 2,4-dinitrophenylhydrazone, which did not lower the m.p. of an authentic sample. [e] Identified in the residual liquid by separate positive tests for hydroxyacetone and a cyanohydrin.

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(21) H. R. Williams and H. S. Mosher, *Anal. Chem.*, **27**, 517 (1955).

(22) A. V. Karyakin and V. A. Nikitin, *Izvest. Akad. Nauk S.S.S.R.*, *Ser. Fiz.*, **17**, 636 (1953); *C. A.*, **48**, 5652 (1954).

(23) All samples of polymeric peroxide were evacuated at a pressure of 0.15–0.25 mm. for several hours at room temperature immediately before use in analyses as well as in all other experiments.

(24) Acetaldehyde and pyruvaldehyde have been separated quantitatively by this method.[16]

(25) C. F. Koelsch and D. Tenenbaum, THIS JOURNAL, **55**, 3049 (1933).

(26) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., Amsterdam, 1939.