[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY OF THE GENERAL ANILINE & FILM CORPORATION]

Role of Oxygen in Vinyl Polymerization. II. Isolation and Structure of the Peroxides of Vinyl Compounds

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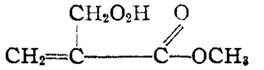
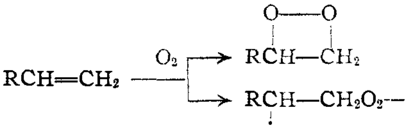
An earlier paper[2] dealt with the general aspects of the effect of oxygen in vinyl polymerization. It was shown that this effect is qualitatively the same both in thermal as well as photopolymerization and that the net result appears to be inhibition due to reaction of active centers with oxygen superimposed on which is a catalysis resulting from the decomposition of the peroxides formed. This paper describes the peroxide isolated from methyl methacrylate[3] and from styrene.

A number of workers have developed hypotheses as to the nature of the peroxide and the mechanism of the inhibition. Price[4] assumed the hydroperoxide structure (I) for methyl methacrylate peroxide.



$$CH_2{=}C(CH_2O_2H){-}C({=}O){-}OCH_3 \quad (I)$$

Heuck[5] postulated the simultaneous formation of a cyclic alkylene peroxide (II) (the Engler–Bach structure) and a one stage adduct (III) of which



(II)

(III)

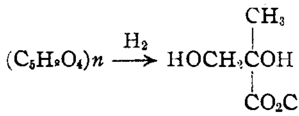
only the latter was a polymerization catalyst except at elevated temperatures. Schulz and Blashke[6] attributed the thermal polymerization of methyl methacrylate to catalysis by monomer peroxide and they attributed the induction period to the time required for building up an appreciable supply of monomer peroxide.

It was recognized at the outset that the peroxide might prove to be either of a monomeric or polymeric nature. The most likely structures seemed to be (a) a monomeric hydroperoxide, (b) a cyclic alkylene peroxide, or (c) a polymeric peroxide which might be formed by interpolymerization of the monomer with oxygen.

A peroxide can be isolated from methyl methacrylate by the evaporation, under reduced pressure, of methyl methacrylate which has been allowed to develop peroxide. The operation is hazardous if conducted much above 40°. The distillate is not peroxidic (provided opportunity is not given for the generation of more peroxide) and contains formaldehyde and methyl pyruvate in addition to recovered methyl methacrylate. The peroxidic residue is obtained as a colorless, gummy substance. It burns in a flame with vigorous puffing but little noise. It has the composition $(C_5H_8O_4)_n$. The possibility of a simple hydroperoxide structure was eliminated when it was found that it is not soluble in water or alkali and has no appreciable amount of active hydrogen.

The peroxide reacts very incompletely in the usual peroxide tests, such as with iodide, arsenite, titanous and ferrous salts, but is a good polymerization catalyst. This behavior is suggestive of a dialkyl peroxide structure. Unlike diethyl peroxide, which is a very fluid liquid, the isolated peroxide is a viscous or gummy substance which strongly suggests a polymeric structure. The intrinsic viscosity in benzene is 0.07 and the cryoscopic molecular weight in dioxane at least 1800.

On hydrogenation the peroxide absorbed only one mole of hydrogen per C_5 unit, indicating that it is not unsaturated, and yielded methyl α,β-dihydroxyisobutyrate as a product.



$$(C_5H_8O_4)_n \xrightarrow{H_2} HOCH_2C(CH_3)(OH)CO_2CH_3$$

Attempts were made to find conditions for the generation of the peroxide which would give a product of the maximum purity. In these experiments, the ultraviolet absorption of the monomer containing the generated peroxide was found to be a useful means of following the purity.

As shown in Fig. 1, the ultraviolet transmission of methyl methacrylate having a given peroxide content by potassium iodide test varies considerably depending on how the peroxide was generated. The maximum transmission was obtained with the product obtained by heating at 40° in the dark. Only a portion of the absorption is attributable to the peroxide as shown by Curve A, Fig. 2, which gives the transmission of the isolated peroxide redissolved in pure methyl methacrylate. Irradiation with ultraviolet light of the isolated peroxide in methanol solution decreases the transmission as shown in Curve B, Fig. 2, which was obtained on dilution with methyl methacrylate. Evidence that the absorption in the region of 3400–3600 Å. is due mainly to degradation products is the fact that the condensate from the isolation of the peroxide absorbs in this region but is not peroxidic. For comparison with the transmission curves of the condensate from different ex-

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(2) Barnes, THIS JOURNAL, 67, 217 (1946).

(3) Presented at the American Chemical Society Meeting at Atlantic City, April 15, 1947.

(4) C. C. Price, *J. Polymer Sci.*, 1, 83 (1946).

(5) I. G. Report, Dec. 18, 1940; (Kuko 136) P. B. 11404.

(6) Schulz and Blashke, *Z. physik. Chem.*, **50B**, 305 (1941); *Z. Elektrochem.*, **47**, 749 (1941).

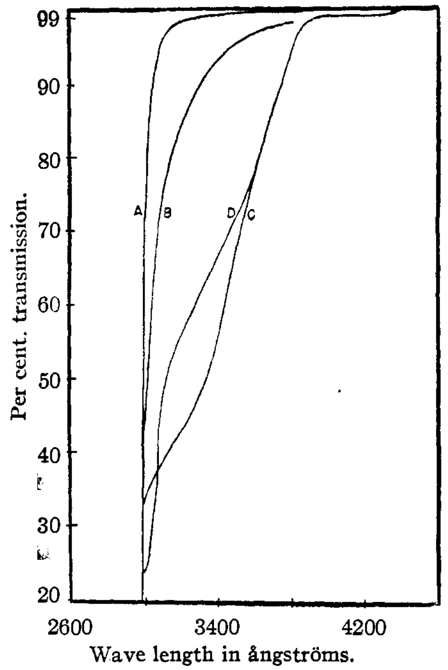

Fig. 1.—Transmission curves for peroxidic methyl methacrylate: A, pure methyl methacrylate; B, C, D, methyl methacrylate containing 0.1% peroxide generated (B) by heating a week at 40°; (C) by heating twenty hours at 65°; (D) by ultraviolet irradiation for ten days at −10°.

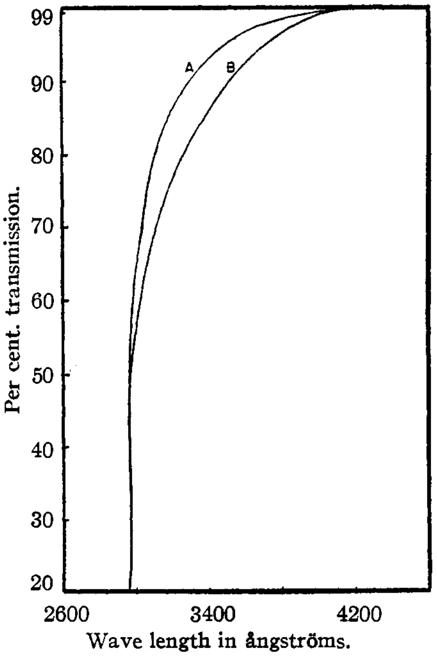

Fig. 2.—Transmission of methyl methacrylate peroxide: A, a solution (0.05%) in pure methyl methacrylate of peroxide isolated by evaporation of peroxidic monomer B (Fig. 1); B, a solution (0.05%) of peroxide isolated as above but irradiated in methanol solution with ultraviolet light at −10° for two hours and then diluted with pure methyl methacrylate.

periments, Fig. 3, there is given the transmission curve of a solution of methyl pyruvate in methyl methacrylate. The destructive distillation of the peroxide yields what is believed to be methyl pyruvate containing a trace of water-soluble peroxide. The other peroxide degradation product, formaldehyde, is detectable by odor in highly peroxidic methyl methacrylate.

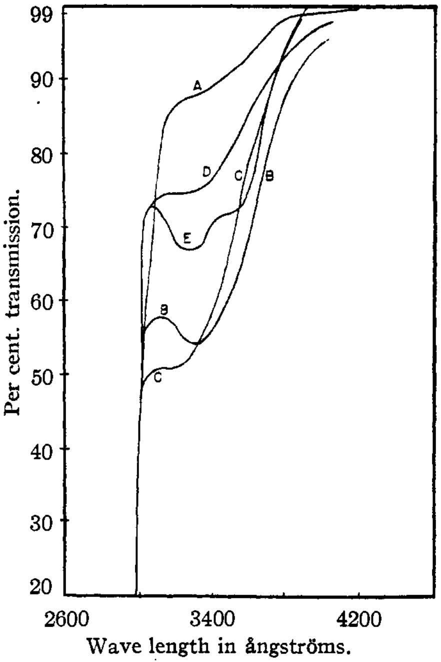

Fig. 3.—Transmission curves for peroxide degradation products obtained from non-peroxidic distillate: A, from B (*cf.* Fig. 1); C, from C (*cf.* Fig. 1); B, from peroxidic (0.1%) methyl methacrylate obtained by generation for two months at room temperature. D and E show transmission of methyl pyruvate in methyl methacrylate solution, D at 0.05% and E at 0.1% (apparently a less pure standard).

In order to gain additional information concerning the nature of this peroxide and to confirm the presence of methyl pyruvate, polarograms were prepared on a number of peroxidic samples. The polarograms were made with a Fisher Elecdropode.

In Fig. 4, Curve 1, is shown a polarogram prepared on the isolated polymeric peroxide. Two distinct waves of nearly equal height are evident; one at a very low potential of about −0.1 volt and the other a drawn out wave at about −0.9 volt. These waves are similar to the conventional waves of oxygen. That the waves are not due to oxygen *per se* is demonstrated by the fact that addition of sodium hydroxide to the cells destroys the waves completely. Oxygen on the other hand produces well-defined waves in alkaline solutions. The height of the two waves together is much smaller than that of an equal concentration by weight of *t*-butyl hydrogen peroxide (Fig. 4, Curves 2 and 3)

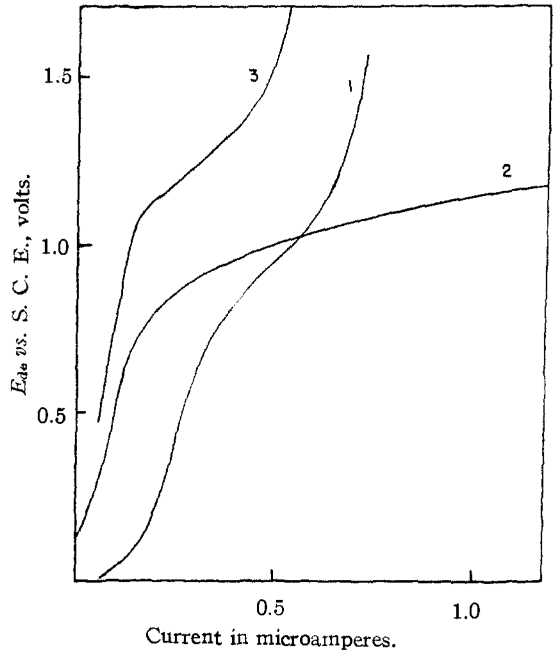

Fig. 4.—Polarograms on methyl methacrylate peroxide, cell containing 10 ml. of acetone, 5 ml. of 0.1 *M* tetramethylammonium bromide and 1 ml. of sample: 1, isolated peroxide 0.1% in acetone; 2, *t*-butyl hydroperoxide (60%) 0.2% in acetone; 3, same as 2 at 0.1 sensitivity.

but is comparable to an equal concentration of methyl pyruvate (Fig. 5, Curve 2). The significance of this latter observation is difficult to assess at present because the diffusion constant of the isolated peroxide and the number of electrons involved in the reduction are both unknown. It is surprisingly large, in agreement with the findings of Bovey and Kolthoff[7] on styrene polyperoxide. However, since hydroperoxide, as demonstrated by *t*-butyl hydrogen peroxide, produces only a single wave at about −1.0 volt it is evident that at least one and probably both of the two waves of the isolated peroxide arises from another structure.

In Fig. 5 evidence is presented to show that pyruvate is an end-product of the oxidation of methyl methacrylate by air, in confirmation of the spectrophotometric results. Curve 2 is a polarogram on methyl pyruvate; Curve 3, a polarogram on isolated peroxide showing little, if any, methyl pyruvate. Curve 1 is a polarogram made at reduced sensitivity on an old sample of peroxidic methyl methacrylate which shows a large pyruvate wave in relation to the height of the peroxide waves. Curve 4 is a polarogram on a solution prepared by heating the isolated peroxide with water. A distinct pyruvate wave appeared and the odor of formaldehyde was noted.

Bovey and Kolthoff[7] reported the isolation of an interpolymer of styrene and oxygen formed during emulsion polymerization. Staudinger[8] prepared polystyrene containing some oxygen but was unable to isolate a 1:1 compound analogous to that which he obtained from unsym. diphenylethylene. It has now been possible to isolate a polymeric peroxide from styrene entirely analogous to that obtained from methyl methacrylate by passing pure oxygen through freshly distilled styrene at 50°. The peroxide analyzed reasonably closely for a 1:1 polymer. It was violently explosive when heated on a spatula in a flame, decomposing by a series of detonations with no flame. The polymer may be hydrogenated with Adams catalyst in ethyl acetate to form phenyl glycol.

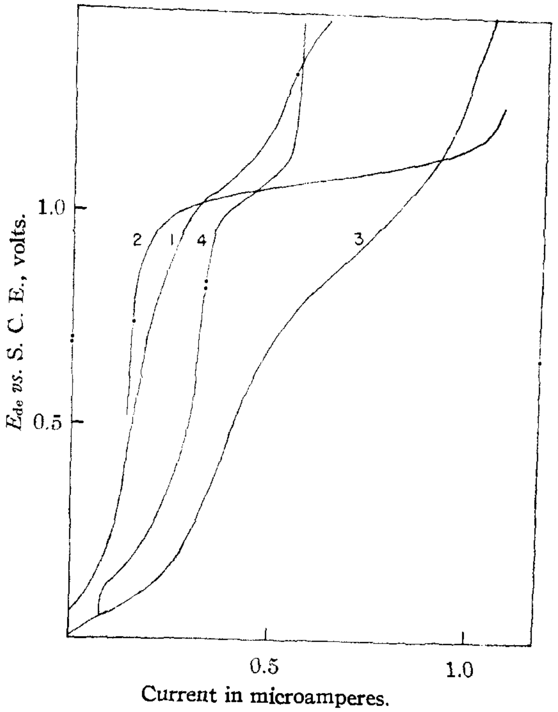

Fig. 5.—Polarograms on methyl methacrylate peroxide, cell containing 10 ml. of acetone, 5 ml. of 0.1 *M* tetramethylammonium bromide and 1 ml. of sample: 1, highly peroxidic aged methyl methacrylate; 2, methyl pyruvate 0.1% in acetone; 3, isolated peroxide 0.1% in acetone; 4, isolated peroxide after heating with water (formaldehyde odor apparent).

Polarograms prepared on the styrene peroxide were similar to those of Bovey and Kolthoff (Fig. 6, Curve 1). However, in buffered acetone solution the odd behavior of the styrene peroxide which they noted is eliminated, and polarograms similar to those obtained with methyl methacrylate peroxide were obtained as shown in Fig. 6, Curve 2.

The polarographic reduction of the polymeric styrene peroxide prompted attempts to reduce the material electrolytically. This was carried out in ethyl acetate and tetramethylammonium bromide containing a small amount of acetic acid. The material was reduced to phenyl glycol and no polymeric styrene was obtained.

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[7] Bovey and Kolthoff, This Journal, 69, 2143 (1947).

[8] Staudinger, *Ann.*, 488, 1 (1931).

It seems clear, therefore, that the isolated peroxides are interpolymers of oxygen with methyl methacrylate or styrene. The former tends to decompose into methyl pyruvate and formaldehyde, the latter into benzaldehyde and formaldehyde. The decomposition probably involves intermediate radicals which account for the ability of the peroxide to act as a polymerization catalyst. The active hydrogen content of 0.04% for the isolated polymeric peroxide of methyl methacrylate and the fact that the reaction with potassium iodide is only about 6% of the expected value may indicate one hydroperoxide end-group for the polymeric peroxide.

It is apparent that the interpolymerization of oxygen with vinyl monomers is a general reaction. This may be represented by typical copolymerization equations[9] where oxygen is treated as a monomer similar to maleic anhydride, for example, which does not polymerize alone, but readily interpolymerizes. Since O_2 radicals do not react with oxygen, only three of the usual four typical copolymerization equations apply (being analogous to, say, a styrene–maleic anhydride interpolymerization)

$$M^* + M \xrightarrow{k_1} M^* \quad (1)$$

$$M^* + O_2 \xrightarrow{k_2} O_2^* \quad (2)$$

$$O_2^* + M \xrightarrow{k_3} M^* \quad (3)$$

Inasmuch as oxygen inhibits ordinary polymerization, reaction (2) is preferred over reaction (1), as maintained in the previous paper.

As pointed out by Bovey and Kolthoff the slow rate of interpolymerization may be accounted for by reaction (3) being much slower than reaction (1). This would agree with a more inefficient chain propagation at step (3) and a lower resulting molecular weight in the oxygen interpolymer formed. Because of the low molecular weight, an equivalent number of active centers are accounted for in only a small per cent. of polymeric peroxide, whereas in the absence of oxygen, the entire mass might be polymerized to a high molecular weight polymer from the same number of active centers.

Another factor limiting the build-up of polymeric peroxides is their decomposition to form aldehydes. In the case of the peroxidation of styrene, little benzaldehyde is formed compared with the peroxide, according to Bovey and Kolthoff. In the case of methyl methacrylate, qualitative polarographic results show that the amounts of pyruvate and peroxide are of the same order. Polarographic results of peroxidic vinyl acetate indicate that much larger amounts of aldehydes than peroxides are obtained when the oxidation is carried out at 40° (Fig. 6, Curve 4).

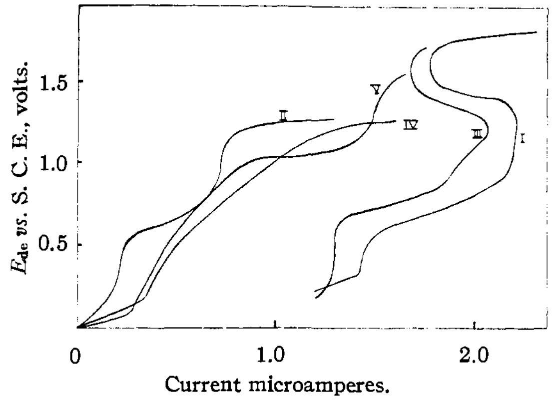

Fig. 6.—Polarograms on vinyl peroxides, drop time in water at 0.0 volt, 5.7 sec., m = 1.20 mg./sec.: 1, cell containing 50 ml. of 58% benzene, 37% ethanol, 5% H_2O, 0.05 M in $(CH_3)_4NBr$ and 1 ml. of 36% isolated styrene peroxide in benzene; 2, cell containing 10 ml. of acetone, 5 ml. of pH 7 buffer (Clark and Lubs), 1 ml. of styrene heated with oxygen at 60° sixteen hours; 3, cell containing 50 ml. of 58% benzene, 37% ethanol, 5% H_2O, 0.05 M in $(CH_3)_4NBr$ and 1 ml. of 5% isolated methyl methacrylate peroxide in benzene; 4, cell containing 10 ml. acetone, 5 cc. of pH 7.0 buffer (Clark and Lubs), 1 ml. of peroxidic vinyl acetate 0.02% by potassium iodide; 5, cell containing 10 ml. of acetone, 5 ml. of pH 7.0 buffer (Clark and Lubs), 1 ml. of methyl methacrylate exposed to air at room temperature for one week in erlenmeyer, sensitivity 2X.

Experimental Part

Methyl Methacrylate Peroxide.—The peroxide was generated by heating purified methyl methacrylate at 40° in the dark for five days. An oxygen stream was introduced to insure an adequate supply of oxygen. No polymer formed and the peroxide content was equivalent by potassium iodide test[8] to 0.04% benzoyl peroxide. The peroxidic monomer (1 liter) was concentrated at 40° bath temperature under reduced pressure to a gummy, colorless residue. Residual solvent was removed at room temperature and 1-mm. pressure overnight; yield, 3.64 g. (0.4%). The product puffed in a flame.

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10; available oxygen, 12.12. Found: C, 47.44; H, 6.74; available oxygen, 11.7; active hydrogen, 0.044 mol.; cryoscopic molecular weight, 1800.

The peroxide can be purified by causing it to oil out of methanol solution on chilling. This was conducted with peroxide which had been generated by allowing the monomer to stand in air at room temperature for two months, developing a peroxide content equivalent by potassium iodide test to 0.01% benzoyl peroxide. A 2-g. yield of product A, which oiled out of methanol, and a 5-g. yield of product B, by evaporation of the methanol, were obtained.

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10. Found: C, 44.91; H, 6.16 for product A. C, 47.17; H, 6.51 for product B.

Concentration of peroxidic monomer at temperatures above 40° is not advised since evaporation at 60° caused an explosion in one instance.

The isolated peroxide is soluble in cyclohexanol and cyclohexane as well as all solvents for polymethyl methacrylate.

The relative viscosity was 1.10 for a 2% solution of the isolated peroxide in dioxane and appeared to be the same whether the peroxide was generated at 40 or 60°. In benzene the relative viscosity was 1.070 at 1% and 1.014 at 0.2%; the intrinsic viscosity, 0.07.

Styrene Peroxide.—One liter of freshly distilled styrene was placed in a polymerization pot and pure oxygen

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(9) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); Alfrey and Lavin, *ibid.*, **67**, 2044 (1945).

bubbled through at 60° for seventy-two hours. The solution was cooled to 40° and evaporated under vacuum to about 200 ml.; 500 ml. of methanol was then added to the residue and approximately 60 g. of oily material separated out. One gram of this material was put in a bottle and placed in a vacuum desiccator overnight, yielding a polymeric solid.

Calcd. for $(C_8H_8O_2)_n$: C, 70.5; H, 5.5. Calcd. for $(C_8H_8)_{20}(O_2)_{19}$: C, 71.41; H, 6.01. Found: C, 71.62; H, 6.33.

The analysis should be considered satisfactory since the substance was violently explosive when heated slightly on a spatula, suggesting that further efforts of purification would be hazardous. A sample prepared in the above manner at 40° showed almost identical analysis (C, 71.59; H, 6.26).

Vinyl Acetate Peroxide.—1200 ml. of freshly distilled vinyl acetate was placed in a resin pot and oxygen was then bubbled through the liquid at 50° in artificial light for seventy hours at room temperature. The resulting solution was evaporated under vacuum in a stream of oxygen and produced 0.5 g. of a sticky semi-solid which exploded vigorously when heated gently in a flame. This material placed in a vacuum desiccator overnight resulted in material with the following analysis: Found: C, 45.41; H, 4.34. Calcd. for $C_4H_6O_4$: C, 44.44; H, 5.55. Calcd. for $C_4H_6O_2$: C, 55.8; H, 6.97.

The anlysis, while not entirely satisfactory, suggests that vinyl acetate forms a peroxide similar to those demonstrated to be polymeric peroxides from methyl methacrylate and styrene. This was further confirmed by polarographic behavior of peroxidic vinyl acetate (Curve 5, Fig. 6).

Available Oxygen.—Since the methods used for the determinations are critical they are reported in detail. The usual procedures for available oxygen, *e. g.*, titanous chloride reduction and iodometry in aqueous dioxane, gave values for available oxygen of 2.5 and 0.6%, respectively. The procedure finally adopted was as follows: A sample (0.05 g.) of the peroxide was dissolved in 5 cc. of glacial acetic acid in an ampule. The ampule was flushed with pure nitrogen and the contents frozen. There was introduced with a hypodermic syringe 1 cc. of colorless, constant boiling hydriodic acid which had been distilled from stabilized (with hypophosphorous acid) hydriodic acid and stored in a brown bottle with a serum cap. The ampule was sealed and heated at 100° for one hour after which period it was chilled, opened and the iodine titrated directly with 0.02 *N* thiosulfate.

Active Hydrogen.—For the active hydrogen determination the concentration of the peroxide was conducted as above except that when the volume had been reduced to 25 cc. this volume was approximately maintained by the addition of dry xylene (250 cc.) during further evaporation (under a stream of dry air). An aliquot (1.478 g.) of the viscous solution finally obtained was evaporated at room temperature and 1-mm. pressure overnight to a 0.714 g. residue, indicating the concentration to be 48.3%: The active hydrogen determination was made[10] on this solution. From 0.5-g. portions there was obtained about 3 cc. of methane at 28° and 745 mm. The sample was diluted with 4 cc. of dry xylene, and 1 cc. of Grignard reagent solution in dibutyl ether was used. The blank was 0.53 cc.; active H, 0.044%.

Molecular Weight.—For the molecular weight measurement a xylene solution of the peroxide was changed to a dioxane solution by portionwise addition of dry dioxane and evaporation at reduced pressure in order to eliminate volatiles other than dioxane. A 10-cc. portion of the purified dioxane was introduced into a cup which was attached by a ground joint to a micro Beckman thermometer and stirred with a commercially available glass-enclosed magnetic stirrer. The melting point was 1.31 ± 0.01°. The peroxide residue was then dissolved in this dioxane and the melting point was 1.27 ± 0.01°. A 5-cc. portion of the solution was evaporated, giving 0.1002 g. of residue. The melting point of the solvent was then rechecked: 1.30°. This indicates a minimum molecular weight of 1880 or about 14 units to the chain as a minimum value for the peroxide.

Hydrogenation of Methyl Methacrylate Peroxide.—Pure methyl methacrylate was heated for fifty hours at 60° in an oxygen stream, developing 0.5% peroxide (by potassium iodide test). The peroxidic monomer (1590 cc.) was evaporated at 40° bath temperature and 60-mm. pressure and dried overnight at 1 mm.; yield 22 g. (1.04%).

Anal. Found: C, 46.11; H, 6.73; available oxygen, 13.2.

The relative viscosity for 0.2% solution in benzene was found to be 1.012.

The 22-g. sample of peroxide was slowly hydrogenated in anhydrous ethyl acetate with platinum oxide catalyst until a negative potassium iodide peroxide test was obtained. The calculated amount of hydrogen was absorbed. There was obtained 13 g. of liquid product, b. p. 105–110° at 18 mm.; $n^{25}D$ 1.4445. There was a tarry residue.

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.77; H, 7.51. Found: C, 44.59; H, 7.28.

A synthetic sample of methyl α,β-dihydroxyisobutyrate, for comparison, was obtained by hydroxylation of methyl methacrylate with *t*-butanolic hydrogen peroxide and osmium tetraoxide; yield, 42%, b. p., 94–96° at 5 mm., $n^{25}D$ 1.4435 found, $n^{25}D$ 1.4438 reported.[11] The ammonium salt, m. p. 124–125.5°, prepared from the isolated and synthetic samples had identical diffraction patterns.[12]

Hydrogenation of Styrene Peroxide.—Ten grams of styrene peroxide, oiled out of methanol and still containing a large amount of methanol, was dissolved in 200 ml. of ethyl acetate; 1 g. of Adams catalyst was added and the mixture was shaken with hydrogen in a Parr hydrogenation apparatus; the pressure dropped 5 pounds. After filtering off the catalyst and evaporating the ethyl acetate on a steam-bath, 3.0 g. of a white crystalline solid remained. This material, recrystallized from benzene, yielded needles of phenyl glycol, m. p. 63–65°; reported for phenyl glycol, 67–68°.[13]

Electrolytic Reduction of Styrene Peroxide.—About 10 g. of polymeric styrene peroxide wet with methanol was dissolved in 600 ml. of ethyl acetate, 50 ml. of water and 15.4 g. of tetramethylammonium bromide. The resulting solution was used as the catholyte for an electrolytic reduction at a stirred mercury cathode. The anolyte contained in a porous cup consisted of 20% sodium hydroxide. The anode was an iron rod. The resulting cell was electrolyzed for seventy-two hours at 0.1 amp. and 20 v. A sample withdrawn as an aliquot still contained peroxide, so 20 ml. of acetic acid was added and the electrolysis continued for an additional one hundred and twenty hours. The resulting catholyte solution was evaporated and yielded no polymeric styrene. Upon dilution of the residue from water there was obtained 5.5 g. of phenyl glycol, m. p. 65–66.5°.

Degradation of the Methyl Methacrylate Peroxide.—A peroxidic distillate was obtained by the careful heating of the oily peroxide at low pressure. This was accomplished by heating a 2.0-g. sample for six hours at 0.1 mm.; the temperature of the mechanically stirred heating-bath was slowly raised to 200°. About 1 g. of a colorless, viscous distillate, b. p. 50–60° (0.1 mm.) was obtained.

Anal. Calcd. for $C_4H_6O_3$: C, 47.06; H, 5.92. Found: C, 46.29; H, 7.03.

1500 cc. of methyl methacrylate, containing peroxide (formed by heating under oxygen in the dark at 40°) equivalent to 0.1% benzoyl peroxide by the potassium iodide test, was evaporated leaving an oily residue. This

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[10] By Dr. C. E. Gould and Miss Patricia Macherly, of this Laboratory.

[11] Glattfeld and Mochel, THIS JOURNAL, **60**, 1011 (1938).

[12] The comparison was made by Dr. S. T. Gross of this Laboratory. The assistance of Dr. C. W. Gould, of this Laboratory, is acknowledged in making derivatives on a micro scale.

[13] Zimcke, *Ann.*, **216**, 294 (1883).

residue was distilled by heating under a pressure of 0.005 mm., the bath temperature being slowly raised to 75°; 1.0 cc. of a colorless, fluid distillate, b. p. 32–35° (0.005 mm.) (132–134° with decomposition at atmospheric pressure) was collected (methyl pyruvate boils at 137°). It burned without puffing and gave a definite but not strong peroxide test with neutral potassium iodide. It was incompletely water-soluble and the water extract was acidic and peroxidic. Since the peroxidic methyl methacrylate before concentration contained no acidic, water-soluble peroxide, this product was assumed to be a secondary product. The residue from the distillation was a nonperoxidic gum. In several attempts to repeat this experiment vigorous explosions occurred.

No clean-cut method was found for reducing the peroxide before isolation. It was attempted to hydrogenate peroxide and monomer both with Raney nickel but the methyl methacrylate could not be quantitatively hydrogenated under mild conditions. Shaking the peroxidic monomer with bisulfite caused instant polymerization in the aqueous phase. Shaking with ferrous salts gave incomplete reduction, as shown by subsequent potassium iodide tests. Liberation of iodine followed by decolorization with thiosulfate was also incomplete with more iodine obtained at each repetition. The addition of hydroquinone to the peroxidic monomer produced on concentration a residue of peroxide contaminated with quinone.

The degradation products in peroxidic methyl methacrylate can be titrated with dichloramine-T using *o*-tolidine as an indicator. There appears to be no reaction of this reagent with the peroxide.

Summary

Evidence is presented that polymeric peroxides are formed when vinyl monomers react with oxygen or air. The structure of these peroxides has been established for methyl methacrylate and styrene. It is suggested that they result from an interpolymerization of the vinyl monomer with oxygen. This has been shown to be consistent with the inhibitory action of oxygen in vinyl polymerizations.

EASTON, PA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XVII. The Reactions of Butenylmagnesium Bromide with Active Hydrogen Compounds

BY K. W. WILSON,[1] JOHN D. ROBERTS[2,*] AND WILLIAM G. YOUNG

Previous work has shown that while the butenyl Grignard reagent has a striking tendency to form α-methylallyl derivatives in a wide variety of coupling and carbonyl addition reactions,[3] hydrolysis with dilute sulfuric acid gives a mixture of butenes. It has been demonstrated that the composition of the butene mixture is independent of the ratio of allylic isomers in the starting butenyl halides[4] and that similar butene mixtures are produced using butenylmagnesium chlorides and bromides.[5] The average composition of the butene mixtures formed in these experiments was 17.2 ± 3.3% *trans*-butene-2, 26.5 ± 1.4% *cis*-butene-2, and 56.4 ± 2.0% butene-1. In contrast to the mixture of butenes produced by dilute aqueous acid hydrolysis, it has been found that cleavage of the Grignard reagent with phenylacetylene gives almost pure butene-1.[3]

In the present investigation, the reaction of the butenyl Grignard reagent has been studied with a wide variety of active hydrogen compounds to see if this type of reaction can be correlated with the earlier formulations of the structure and reaction mechanisms of the butenylmagnesium halides.[3]

Experimental Results and Discussion

The butene mixtures were analyzed with a Beckman IR-2 Infrared Spectrophotometer. Considerable difficulty was experienced in completely removing the butenes from the reaction mixtures. Consequently, the values for butene-1 may be too high by as much as 5%. Analyses were made in duplicate in nearly all experiments and, in many cases, two or more separate runs were made with each active hydrogen compound. The results are given in Table I.

It is apparent that in the cleavage of butenylmagnesium bromide the nature of the active hydrogen compound employed has a marked influence on the composition of the resulting butene mixtures. Water and alcohols give comparable butene mixtures. Carboxylic acids and hydrogen chloride give considerably more butene-1 than alcohols or water. No regular variation of the compositions of the mixtures with acid strength is apparent. Ammonium iodide, dibenzenesulfonylmethane, benzhydryl mesityl ketone and phenylacetylene[3] give quite different butene mixtures, which are unlike those obtained with water, acids or alcohols. Considerably less butene-1 is formed in the absence of a solvent for the Grignard reagent but little variation in composition is noted on substitution of dibutyl ether, benzene or heptane for diethyl ether.[6]

In our opinion, the results of the present study are not inconsistent with our earlier formulation of the Grignard reagent as crotylmagnesium bromide.[3] In general, the reactions of the butenylmagnesium halides have considerable resemblance

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[1] Present address, Chemistry Department, West Virginia University.

[2] Present address. Chemistry Department. Massachusetts Institute of Technology.

[3] Young and Roberts, THIS JOURNAL, 68, 1472 (1946). This paper gives references to earlier work on the coupling and carbonyl addition reactions.

[4] Young, Winstein and Prater, *ibid.*, 58, 289 (1936).

[5] Young and Eisner, *ibid.*, 63, 2113 (1941).

[6] Considerably greater variations with benzene and heptane might be found if it were possible to remove all of the coördinated diethyl ether from the Grignard reagent by distillation.