[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, OHIO UNIVERSITY]

The Kolbe Electrolysis as a Source of Free Radicals in Solution II. The Polymerization of Some Vinyl Monomers[1]

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The electrolysis of an aqueous solution of potassium acetate in the presence of vinyl acetate, methyl methacrylate or vinyl chloride produced the respective polymers. When the electrolysis with vinyl acetate as the monomer was conducted in a divided cell, polymer was found only in the anode compartment. The electrolysis of potassium acetate-2-C^{14} in the presence of either vinyl acetate or methyl methacrylate produced radioactive polymers. These results indicate that acetoxy or methyl free radicals produced during the electrolysis serve as polymerization initiators.

Introduction

Over a period of years considerable interest has been shown in electrolytic methods of initiating vinyl polymerizations. Dineen, Schwan and Wilson[2] found that acrylic acid and methacrylic acid as well as their respective methyl esters were polymerized at the cathode when subjected to electrolysis in dilute sulfuric acid solutions. Similar results were reported by Parravano[3] who established that polymerization resulted from hydrogen atoms formed at the cathode. Kolthoff and Ferstandig[4] have reported the polymerization of acrylonitrile initiated by the electrolysis of ferric ion in an oxidation–reduction system. Recently Yang, McEwen and Kleinberg[5] polymerized styrene during the electrolysis of sodium iodide in pyridine using magnesium electrodes.

Evidence in the literature[5a,6] and our own experience[1] suggested the Kolbe electrolysis as a useful source of free radicals for the initiation of vinyl polymerization. It has been reported that the electrolysis of sodium acetate in acetic acid solutions of styrene produced a low molecular weight polystyrene oil.[6] However, attempts to polymerize styrene or acrylonitrile during the electrolysis of potassium laurate have been reported to fail.[7] As a part of a study of the Kolbe electrolysis as a source of free radicals in solution we have examined the reactions proceeding during the electrolysis of potassium acetate solutions in the presence of each of the monomers: vinyl acetate, methyl methacrylate and vinyl chloride.

Discussion

The polymerization of vinyl acetate was carried out by electrolyzing a rapidly stirred mixture of vinyl acetate and dilute potassium acetate using smooth platinum electrodes. After several hours the reaction ceased due to the deposition of polymer on the electrodes. The tacky polymer mixture was recovered from the flask with the aid of a solvent. Removal of the solvent and any unreacted monomer gave a rather hard mass of buff colored polyvinyl acetate.

One referee has pointed out the possibility that oxygen might exert a considerable influence on the course of the polymerization, citing the recently published work of Mayo, Miller and Russell[8] on the potent inhibitory effects of oxygen on the polymerization of vinyl acetate. While no examination of the evolution of oxygen was made in this study, there is considerable evidence that only very small amounts of oxygen are formed under the conditions employed here.[9] In one experiment nitrogen was bubbled rapidly through the efficiently stirred mixture both prior to and during the electrolysis. The polymer so formed was water-white and of only slightly lower intrinsic viscosity than that produced above. While no analyses were conducted to determine the presence of excess oxygen in the polymer, the hydrolysis and reacetylation of the polymer produced in the presence of oxygen in the atmosphere gave back material of the same intrinsic viscosity as the starting material suggesting that no large number of peroxide links were to be found in this material. Thus, while the intervention of oxygen cannot be ruled out completely, it is evident that it plays no significant role in determining the course of the reaction.

The hardness of the polymer ($[\eta]^{25}$ 0.80 100 ml./g. (acetone)) suggested that it might be highly cross-linked or crystalline in nature. The latter possibility was not unreal, for the electrolysis of potassium acetate in the presence of butadiene has been shown to lead to the formation of 3-hexene of *trans* configuration only. The hydrolysis and reacetylation experiment described above gave back material with the same intrinsic viscosity as the starting material, thus ruling out cross-linking as any significant factor. An X-ray powder picture of the polymer showed the hazy pattern characteristic of an amorphous substance. Hence, the polymer had no crystallinity and was not isotactic. Perhaps the brittleness could be attributed to a rather high distribution of long chains in the polymer; however, this matter was not further investigated.

Electrolytic methods of initiating vinyl polymerization are attractive because by controlling

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(1) For the preceding paper in this series see W. B. Smith and H.-G. Gilde, THIS JOURNAL, **81**, 5325 (1959).

(2) E. Dineen, T. C. Schwan and C. L. Wilson, *Trans. Electrochem. Soc.*, **96**, 226 (1949).

(3) G. Parravano, THIS JOURNAL, **73**, 628 (1951).

(4) I. M. Kolthoff and L. L. Ferstandig, *J. Polymer Sci.*, **6**, 563 (1951).

(5) J. Y. Yang, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **79**, 5834 (1957).

(5a) R. V. Lindsey, Jr., and M. L. Peterson, *ibid.*, **81**, 2073 (1959).

(6) (a) S. Goldschmidt and E. Stöckel, *Chem. Ber.*, **85**, 630 (1952); (b) S. Goldschmidt, *Angew. Chem.*, **69**, 132 (1957).

(7) H. Z. Friedlander, S. Schwan and C. S. Marvel, *J. Electrochem. Soc.*, **100**, 409 (1953).

(8) F. R. Mayo, A. A. Miller and G. A. Russell, THIS JOURNAL, **80**, 2500 (1958).

(9) (a) S. N. Shukla and O. J. Walker, *Trans. Faraday Soc.*, **27**, 35 (1931); (b) S. Glasstone and A. Hickling, *J. Chem. Soc.*, 820 (1936); (c) A. Hickling and J. V. Westwood, *ibid.*, 1039 (1938).

the electrolysis current one may control the generation of free radicals in the system. It would be expected that at higher concentrations of initiating radicals the processes of chain termination either by combination of growing polymer chains or by termination with a radical produced by the electrolysis would increase with a resultant lowering of the intrinsic viscosity. The initial experiment was conducted at an average current of 2.5 amperes passing through the cell. As mentioned above, the polymer produced had an intrinsic viscosity of 0.80 in acetone. When the current was dropped to 0.5 ampere the time to current drop was greatly extended. The polymer produced showed a significant increase in intrinsic viscosity to 0.99. In view of the fact that the molecular weight of polyvinyl acetate is largely controlled by chain transfer with the monomer[10] it might reasonably be expected that the effect would be more pronounced in polymerizations where such is not the case.

In order to answer the question of whether or not the above polymerizations were being initiated by methyl and acetoxy free radicals produced at the anode and not by some process occurring at the cathode as previously observed,[2,3] two sets of experiments were carried out. When the electrolysis was conducted in an H-cell with the electrode compartments separated by a glass frit it was found that polyvinyl acetate formed only in the anode compartment. Furthermore, if the electrolysis was conducted using potassium acetate-2-C^{14} as the electrolyte the polymer formed was radioactive. The time for this electrolysis was 15.5 hours. Recognizing the possibility of acetate exchange between the electrolyte and the polymer, a sample of non-radioactive polymer dissolved in vinyl acetate was stirred for three days with a sample of electrolyte. The recovered polymer had less than one-fourth of the activity of material produced above. These results clearly indicate the initiation to be *via* the radicals produced during the electrolysis of the acetate ion. Similar findings will be mentioned below for the polymerization of methyl methacrylate.

The polymerization of methyl methacrylate was carried out in an analogous fashion to that used for vinyl acetate. A hard, water-white polymer was formed in a somewhat lower yield than that observed for vinyl acetate. Since the reaction stopped when the polymer coated the electrode this may simply reflect a lower solubility of the polymer in the monomer in this case. When the electrolysis was carried out using radioactive potassium acetate, the polymer formed was also radioactive in keeping with the observations mentioned previously for the polymerization of vinyl acetate.

Finally, an attempt was made to polymerize vinyl chloride by this procedure. The electrolyte was diluted with ethanol to prevent its freezing during the reaction and to increase the solubility of the monomer. After a number of hours the reaction was stopped as no visible polymer formation had occurred. A small amount of polymer was obtained from the reaction. This material was not completely soluble in acetone suggesting that cross-linking may occur to some extent in this case.

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Experimental

Viscosities were determined in an Ostwald viscometer mounted in a thermostated bath held at 25.0 ± 0.1°. Intrinsic viscosities were determined by the usual graphical plots and are expressed in units of 100 ml./g.

Polymerization of Vinyl Acetate.—The reaction was carried out in a flask fitted with a condenser, stirrer and a pair of smooth platinum electrodes 1.5″ square spaced 0.25″ apart. The flask was cooled with an ice–water-bath. The reaction vessel was charged with 100 g. of freshly distilled vinyl acetate, 100 g. of potassium acetate and 500 ml. of water. The mixture was stirred vigorously, and a current of 2.5 amperes was passed through the cell. After about 6 hours the current suddenly fell as the electrodes and flask became coated with thick, lumpy polymer. The current was cut off, and the electrolyte was decanted from the polymer. Residual polymer was dissolved from the flask by acetone. The acetone and unreacted monomer were removed from the polymer under reduced pressure at 50–60°. The yield of polyvinyl acetate, recovered as buff colored lumps, was 38 g., $[\eta]^{25}$ 0.80 (acetone), m.p. 127–132°. An X-ray powder photograph of this material produced the usual hazy pattern of an amorphous substance.

A sample of this polymer was hydrolyzed to polyvinyl alcohol by heating in ethanolic potassium hydroxide and pouring the mixture into water. The hydrolyzed material, in contrast to the initial sample, failed to give a positive ester test with hydroxylamine–ferric chloride reagent. The polyvinyl alcohol then was acetylated in acetic anhydride–pyridine. The recovered polyvinyl acetate had, within experimental error, the same intrinsic viscosity as that reported above.

Several experiments related to the above were carried out. In one the current was maintained at 0.5 ampere. Twenty-five hours was required before polymer formation stopped the electrolysis. The yield of product was 30.5 g., $[\eta]^{25}$ 0.99 (acetone).

In another experiment the apparatus was continuously flushed with nitrogen throughout. The electrolysis was carried out at 1.5 amperes for 13.5 hours before thickening occurred. The electrolysis product was separated from the polymer–monomer mixture, and the monomer was removed under reduced pressure. The product, 17.5 g., was water-white, $[\eta]^{25}$ 0.49 (acetone).

Finally, a polymerization was carried out in an H-cell with a fritted glass partition. Each side was cooled in ice-water and stirred with a magnetic stirrer. Each side was charged with 10 ml. of freshly distilled vinyl acetate, 20 g. of potassium acetate and 100 ml. of water. The electrolysis was conducted at 1.0 ampere for 5 hours. The oily layer was separated from electrolyte on each side, and the monomer removed at reduced pressure. No polymer was found in the material from the cathode cell. About 1 g. of soft, white polymer was isolated from the anode compartment.

Polymerization of Methyl Methacrylate.—The polymerization of methyl methacrylate was carried out as described above. The reactor was charged with 100 g. of freshly distilled methyl methacrylate, 100 g. of potassium acetate and 550 ml. of water. The current was maintained at 2.5 amperes for five hours at which time a drop in the field voltage of the d.c. generator caused the current to drop to 1.5 amperes. An additional 4 hours at the latter value led to the formation of polymer in the reaction vessel. Benzene was used to remove the polymer from the reaction vessel. The solvent and unreacted monomer were removed at reduced pressure to yield hard, white lumps of polymethyl methacrylate; yield 15.5 g., m.p. 178–185°, $[\eta]^{25}$ 0.89 (methyl ethyl ketone).

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(10) A. J. Buselli, M. J. Dindemann and C. E. Blades, *J. Polymer Sci.*, **28**, 485 (1958).

Polymerization of Vinyl Chloride.—The reactor described above (Dry Ice condenser) was charged with 120 ml. of vinyl chloride, 100 g. of potassium acetate, 600 ml. of water and 100 ml. of ethanol. The electrolysis was conducted for 11.5 hours at 1 ampere. No visible change was noted. The vinyl chloride was allowed to boil off, and the white precipitate of polymer was collected by filtration; yield 0.65 g. The material was not totally soluble in methyl ethyl ketone and 0.15 g. of gel material was filtered off. The intrinsic viscosity of the soluble portion was 0.30 (methyl ethyl ketone, 25°).

Polymerizations with Potassium Acetate-2-C^{14}.—The method of radiocarbon analysis has been described elsewhere.[11] The electrodes (each one inch square of smooth platinum spaced *ca.* 1/8'' apart) were inserted by long leads through the condenser. The reaction mixture consisted of 40 ml. of vinyl acetate, 5 g. of potassium acetate-2-C^{14} (1.209 ± 0.016 mc./mole), and 10 ml. of water. The electrolysis was run with stirring for 15.5 hours at 0.5 ampere. The polymer was recovered as described above. Purification was effected by precipitating the polymer from acetone solution by pouring the latter into water. This process was repeated three times. The yield of polymer was 0.108 g., $[\eta]^{25}$ 0.20 (acetone), radioactivity $3.89 \pm 0.09 \times 10^{-7}$ mc./mg.

A measure of the amount of acetate exchange was carried out by stirring a mixture of non-radioactive polyvinyl acetate dissolved in vinyl acetate monomer with a solution of potassium acetate-2-C^{14} made up as nearly as possible as the solution used in the electrolysis experiment. The mixture was stirred at room temperature for three days. The polymer was recovered and purified as above; radioactivity $8.52 \pm 0.17 \times 10^{-8}$ mc./mg.

The polymerization of methyl methacrylate was carried out as above but in a 100-ml. flask. A mixture of 15 ml. of methyl methacrylate, 5 g. of potassium acetate-2-C^{14} (1.209 ± 0.016 mc./mole), and 70 ml. of water was electrolyzed at 1.0 ampere for 4.25 hours. The polymer was recovered and purified as above; yield 0.13 g., $[\eta]^{25}$ 0.79 (methyl ethyl ketone), radioactivity $1.18 \pm 0.07 \times 10^{-6}$ mc./mg.

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[11] W. B. Smith, R. E. Bowman and T. J. Kmet, THIS JOURNAL, **81**, 997 (1959).

[CONTRIBUTION NO. 1549 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

1-Methoxyvinyl Esters.[1] I. Preparation and Properties

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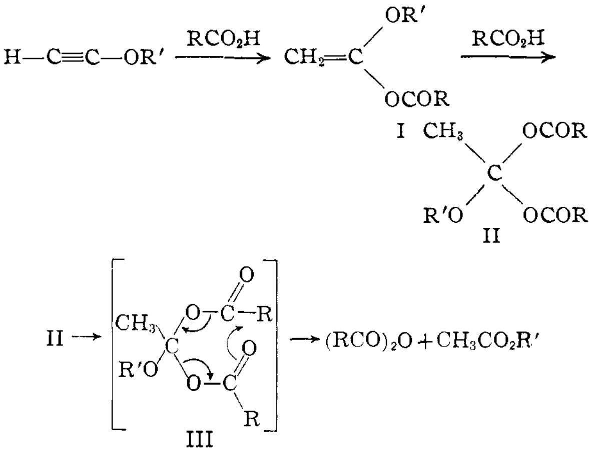
Methods are described for the preparation, in good yield of a number of 1-methoxyvinyl esters from the reaction of methoxyacetylene with the corresponding carboxylic acids. Some of the physical and chemical properties of these compounds are reported.

The reactions of alkoxyacetylenes have been extensively investigated in recent years, mainly by Arens and co-workers.[3] It was found that one mole of methoxy- or ethoxyacetylene reacts rapidly at room temperature with two moles of a variety of carboxylic and other acids to produce the corresponding anhydrides in good yield.[4] This reaction has been assumed to occur by the intermediate formation of 1-alkoxyvinyl esters (I) and 1-alkoxyethylidene diesters (II), anhydride formation resulting from the decomposition of II *via* the cyclic transition state III.[4c]

Early attempts to isolate the intermediate I in the case of the reaction of acetic acid with ethoxyacetylene were unsuccessful using (a) an equimolar amount[4c] and (b) an excess[4a] of ethoxyacetylene. On the other hand, Arens has recently reported the facile formation of I, R = CCl_3, R' = C_2H_5, as well as I, R = $CHCl_2$, R' = C_2H_5, from trichloroacetic acid and dichloroacetic acid, respectively, although monochloroacetic acid failed to yield I, R = CH_2Cl, R' = C_2H_5.[5]



We were interested in methods for the preparation of 1-alkoxyvinyl esters because of their potential usefulness as reactive acylating agents in the synthesis of unsymmetrical anhydrides and peptides.[1] This paper describes our studies with methoxyacetylene.[6]

It was found that 1-methoxyvinyl trifluoroacetate was rapidly formed in good yield (78%) from the reaction of trifluoroacetic acid with a slight excess of methoxyacetylene in methyl chloride solvent. Likewise, in agreement with Arens' findings,[5] 1-methoxyvinyl trichloroacetate appeared

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[1] For a preliminary communication on this subject, see H. H. Wasserman and P. S. Wharton, *Tetrahedron*, **3**, 321 (1958). This paper is abstracted from the Doctoral Dissertation of P. S. Wharton, submitted to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1959.

[2] Procter and Gamble Fellow, 1957–1958.

[3] See J. F. Arens and H. C. Volger, *Rec. trav. chim.*, **77**, 1170 (1958), and earlier papers in this series.

[4] (a) J. F. Arens and P. Modderman, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **53**, 1163 (1950); *C. A.*, **45**, 6152 (1951); (b) J. F. Arens and T. Doornbos, *Rec. trav. chim.*, **74**, 79 (1955); (c) G. Eglinton, E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

[5] R. Broekema, S. van der Werf and J. F. Arens, *Rec. trav. chim.*, **77**, 258 (1958).

[6] An improved preparation of methoxyacetylene on a two-molar scale, by a modification of the published procedure for ethoxyacetylene, *Org. Syntheses*, **34**, 46 (1954), is described in detail in the Experimental section. See also the procedure for the preparation of ethoxyacetylene described by I. N. Nazarov, Zh. A. Krasnaia and V. P. Vinogradov, *J. Gen. Chem. U.S.S.R.*, **28**, 451 (1958).