

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

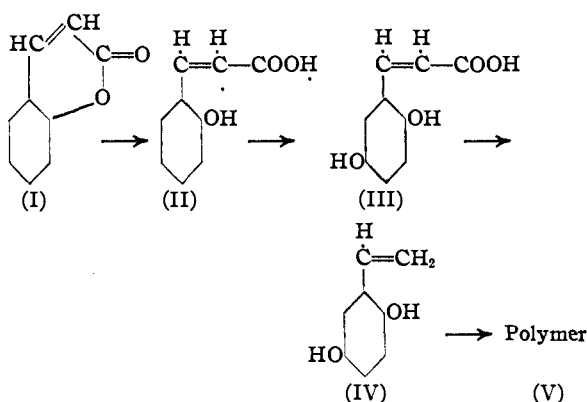
Electron Exchange-Polymers. II. Vinylhydroquinone Monomer and Polymer

BY IVOR H. UPDEGRAFF AND HAROLD G. CASSIDY

Introduction

A previous paper¹ set forth the requirements for an electron exchange-polymer and showed that these requirements are met by a polymerized vinylhydroquinone. This paper discusses, and describes the preparation and properties of, vinylhydroquinone and polymerized vinylhydroquinone.

The synthetic scheme is illustrated by structures I to V



Coumarin (I) was converted to *o*-coumaric acid (II) by refluxing it with sodium ethylate according to the directions of Ebert.² The *o*-coumaric acid was then converted to 2,5-dihydroxycinnamic acid (III) by treating it with potassium persulfate according to the method of Neubauer and Flatow.³ The decarboxylation of 2,5-dihydroxycinnamic acid was carried out by heating the free acid under reduced pressure in a sublimation apparatus to a temperature slightly above its melting point. The vinylhydroquinone (IV) produced by the loss of carbon dioxide sublimed as it was formed together with some of the unchanged acid.

For polymerization, the vinylhydroquinone was sealed in a glass tube under reduced pressure and heated to 125° for many hours without added catalyst. Within the first minutes of heating the monomer melted to a pale amber, mobile liquid. This became very viscous within the course of an hour. After cooling, the polymer was extracted with hot benzene to remove unchanged or slightly polymerized monomer.

Vinylhydroquinone has not been previously described. It is a colorless crystalline solid which melts at 111°. Its identity was established by ultimate analysis as well as by catalytic hydrogenation to the known compound ethylhydroquinone.

Polymerized vinylhydroquinone is a pale amber, brittle solid. It is soluble in polar organic solvents and insoluble in benzene. In the presence of water it becomes soft and tacky. An attempted catalytic hydrogenation failed to reveal unsaturation. The oxidation equivalent determined by mild oxidation is that which would be expected for the conversion from the hydroquinoid to the benzoquinoid form of a polymer in which the functional hydroxyl groups are not involved in cross-linking. The polyquinone so produced is a reddish-orange solid, insoluble in water but easily soluble in most organic solvents, and attacked by strong oxidizing agents.

Experimental

***o*-Coumaric Acid.**—Coumarin (E. K. Co.) was converted to *o*-coumaric acid by refluxing it for four hours with sodium ethylate, diluting with water, removing most of the solvent *in vacuo*, and neutralizing with concentrated hydrochloric acid. The purified acid was obtained in a yield of 82%; m. p. 207–208° with dec.; neutralization equivalent calcd. 164, found 162.5.

2,5-Dihydroxycinnamic Acid.—Coumaric acid (93 g., 0.57 mole) was dissolved in a solution of 160 g. of sodium hydroxide in 3 liters of water. To this solution was added 170 g. of potassium persulfate as a slurry in 1 liter of water. The solution was swirled until all the persulfate had dissolved and was then allowed to stand for twenty-four hours. Concentrated hydrochloric acid was added in small amounts until the solution was red to methyl orange. It was then extracted with ethyl ether in a continuous extractor for twenty-four hours. The extract (35 g.) consisted principally of unchanged coumaric acid. The remaining solution was treated with 600 ml. of concentrated hydrochloric acid and the extraction continued for one week. The crude extract (54 g.) which remained after the evaporation of the ether was puddled with fresh ether and the solid retained on a Büchner funnel. The solid (crude 2,5-dihydroxycinnamic acid) was further purified by treatment with activated charcoal in boiling water. It crystallized from water in the form of needles. Even after repeated crystallization the acid retained a pale green color; yield 23 g. (0.13 mole, 23%); m. p. 208° with decomposition; neutralization equivalent calcd. 180, found 178.5.

Vinylhydroquinone.—2,5-Dihydroxycinnamic acid (5 g., 0.028 mole) was charged to a vacuum sublimation apparatus, the pressure reduced to approximately 0.01 mm., and the bulb heated in an oil-bath to 200°. Decarboxylation began at this temperature. The temperature was then slowly raised to 220° over a period of one hour. When the apparatus had cooled the crude sublimate was scraped from the cold surface. It was mixed with about 50 ml. of benzene and the mixture heated to boiling. The warm solution was then filtered to remove unchanged 2,5-dihydroxycinnamic acid which had sublimed with the vinylhydroquinone. On cooling the solution vinylhydroquinone separated as colorless needles; yield 1.45 g. (0.01 mole, 38%), m. p. 111°, cor.

Anal. Calcd. for C₉H₈O₂: C, 70.59; H, 5.92. Found: C, 70.17, 70.61; H, 5.83, 5.99.

Vinylhydroquinone (0.0934 g., 0.000686 mole) was dissolved in 15 ml. of ethyl acetate and treated with hydrogen at atmospheric pressure in the presence of Adams catalyst. Volume of hydrogen adsorbed (S.T.P.) 16.4 ml., calcd. 15.4. The hydrogenation mixture was decanted from the

(1) H. G. Cassidy, *THIS JOURNAL*, **71**, 402 (1949).

(2) G. Ebert, *Ann.*, **226**, 347 (1884).

(3) O. Neubauer and I. Flatow, *Z. physiol. Chem.*, **52**, 375 (1907).

catalyst and the ethyl acetate removed under reduced pressure. The residue was dissolved in about 3 ml. of warm benzene and allowed to cool. Colorless crystals were obtained, m. p. 115°. Ethylhydroquinone⁴ melts at 113–114°. This material was titrated with ceric sulfate: oxidation equivalent calcd. 69.08, found 70.5.

Polymerized Vinylhydroquinone.—Approximately 1 g. of vinylhydroquinone was placed in a glass tube, evacuated to approximately 1 mm. and sealed off. The sealed capsule was placed in an oven at 125° for one hundred hours. After cooling, the brittle solid which had formed was powdered and treated three times with boiling benzene, the successive portions of benzene being decanted from the insoluble residue. The product was an amber, brittle solid, insoluble in benzene, soluble in alcohol, acetic acid, ether and acetone, somewhat soluble in boiling water, becoming soft and tacky in cold water. This material was titrated with bromine in 90% acetic acid.⁵ Oxidation equivalent calcd. 68.06, found 68.

Oxidations were carried out⁴ on polymerized vinylhydroquinone, hydroquinone and a number of related substances.

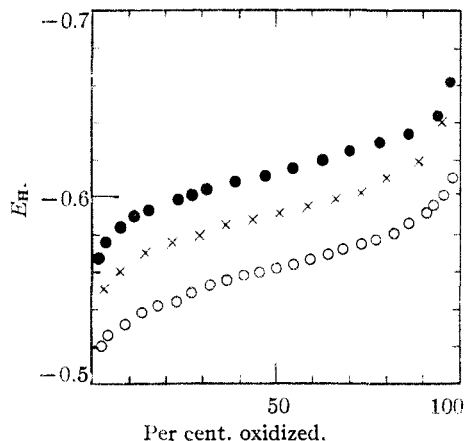


Fig. 1.—Oxidation of hydroquinone, vinylhydroquinone and ethylhydroquinone: E_H , potential in volts referred to the normal hydrogen electrode; ●, data for hydroquinone, pH 1.3, no. (1) in experimental part; X, data for vinylhydroquinone, pH 1.3, (7); O, data for ethylhydroquinone, pH 1.26, (4).

Figure 1 shows the data for hydroquinone, vinylhydroquinone and ethylhydroquinone oxidized in solution in 50% acetic acid; Fig. 2 shows the data for hydroquinone, ethylhydroquinone, and dispersed polymerized vinylhydroquinone; Fig. 3 shows the curve for dispersed polymerized vinylhydroquinone from Fig. 2, and the curve for a mixture of hydroquinone and ethylhydroquinone. Pertinent data from these titrations and those reported previously¹ are gathered below. E_0 is the mid-point potential referred to the normal hydrogen half-cell and calculated to a pH of 0. E_1 is the index potential, the potential difference between 50% oxidation and 25% (or 75%) oxidation. δ is the slope at the midpoint of the titration curve, and was determined graphically from our data. δ is given in millivolts per unit of μ , where μ is -1 at 0% oxidation, 0 at 50% oxidation and $+1$ at 100% oxidation. The implications of these values are given in Paper I.¹ The nomenclature is that of Michaelis.⁶

Oxidation of Hydroquinone.—(1) (Fig. 1) 7.76 mg. in 10 ml. 50% acetic acid, oxidized with potassium dichromate in 50% acetic acid. Final pH 1.3; T ca. 28°.

(4) T. B. Johnson and W. W. Hodge, *THIS JOURNAL*, **35**, 1014 (1913).

(5) L. Michaelis and E. S. Hill, *ibid.*, **55**, 1481 (1933).

(6) L. Michaelis, *Chem. Revs.*, **16**, 243 (1935); L. Michaelis and M. P. Schubert, *ibid.*, **22**, 437 (1938); L. Michaelis, *Ann. New York Acad. Sci.*, **40**, 39 (1940).

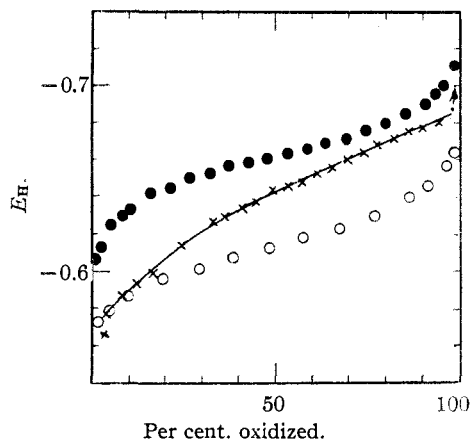


Fig. 2.—Oxidation of polymerized vinylhydroquinone compared with that of hydroquinone and ethylhydroquinone: E_H , potential in volts referred to the normal hydrogen electrode; ●, data for hydroquinone, pH 0.54, no. (2) in experimental part; X, data for polymerized vinylhydroquinone, pH 0.54 to 0.50, (8); O, data for ethylhydroquinone, pH 0.5, (5).

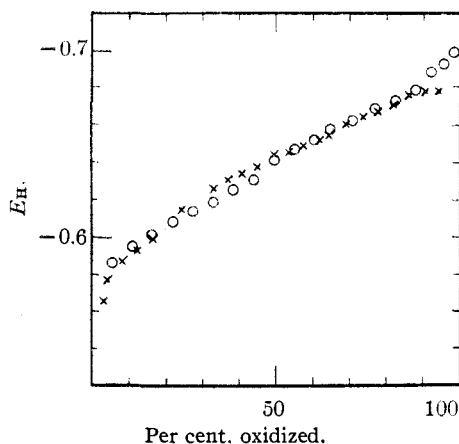


Fig. 3.—Comparison of oxidation of polymerized vinylhydroquinone with oxidation of a mixture of hydroquinone and ethylhydroquinone: E_H , potential in volts referred to the normal hydrogen electrode; X, data for polymerized vinylhydroquinone, as in Fig. 2; O, data for a mixture of hydroquinone and ethylhydroquinone, pH 0.54, (10). The correspondence of the two curves is probably fortuitous; the shapes are of chief interest.

E_0 -0.697 ; E_1 13 and 14 mv.; δ 26 mv. per unit of μ . (2) (Fig. 2) 14.777 mg. in 10 ml. sulfuric acid-potassium sulfate buffer pH 0.53 oxidized with ceric sulfate, pH 0.54. E_0 -0.692 ; E_1 13, 14 mv.; δ 24 mv./ μ . (3) (Fig. 1, Paper I) 10.043 mg. in 10 ml. 90% acetic acid (pH 0.0) titrated with bromine in 90% acetic acid. Final pH ca. -0.4 ; T 24°. E_0 -0.697 ; E_1 20, 14 mv.; δ 27 mv./ μ .

Oxidation of Ethylhydroquinone.—(4) (Fig. 1) 17.311 mg. in 10 ml. 50% acetic acid, with dichromate. Final pH 1.26; T 20°. E_0 -0.636 ; E_1 16, 14 mv.; δ 27 mv./ μ . (5) (Fig. 2) 9.5 mg. in 10 ml. sulfuric acid-potassium sulfate buffer, with cerate. pH 0.5; T 26°. E_0 -0.644 ; E_1 14, 15 mv.; δ 23 mv./ μ . (6) (Fig. 1, Paper I) 12.918 mg. in 10 ml. acetic acid-water, pH -0.45 . Titrated with bromine in same solvent. Final pH ca. -0.6 . E_0 ca. -0.65 ; E_1 22, 22 mv.; δ ca. 42 mv./ μ .

Oxidation of Vinylhydroquinone.—(7) (Fig. 1) 5.13 mg. in 10 ml. 50% acetic acid, with dichromate. Final pH 1.3, E_0 -0.667 ; E_1 13, 12 mv.; δ 23 mv./ μ .

Oxidations of Polymerized Vinylhydroquinone (PVH).—(8) (Figs. 2 and 3) 14.871 mg. in 0.15 ml. acetic acid mixed with 10 ml. sulfuric acid-potassium sulfate buffer containing 2.44 mg. of albumin.¹ pH 0.54 to 0.5; T 25°. E_0 -0.673 ; E_1 28 and 22 mv.; " δ " 45 mv./ μ . (9) (Fig. 1, Paper I). 12.094 mg. in 10 ml. acetic acid-water, pH -0.45 , with bromine in the same solvent. Final pH -0.6 ; T 23°. E_0 -0.679 ; E_1 32, 35 mv.; δ ca. 70 mv./ μ . A number of titrations of PVH have been carried out with and without albumin and in solution and dispersed. The mid-point potentials (E_m) have hardly ever been more than 10 mv. different, but the slopes have varied considerably. The curves given are typical ones. The titration behavior of this polymer needs considerable study. The amount of albumin used was from 2 to 3 mg. in these experiments. In a separate experiment this was found equivalent to 0.052 to 0.08 ml. of 0.0279 N cerate at pH 0.5, with an E_m of -0.680 v. The effect of this small amount of albumin seemed to be to render a little less sharp the end-point of the titration, the E_m of the albumin lying usually well above that of the other reductant.

Oxidation of Mixture.—(10) (Fig. 3) 6.832 mg. (0.0696 me.) hydroquinone and 4.162 mg. (0.0603 me.) ethylhydroquinone in 1 ml. of acetic acid mixed with 10 ml. of sulfuric acid-potassium sulfate buffer and titrated with cerate. Final pH 0.54; T 27°; E_0 -0.672 ; E_1 29, 27 mv.; " δ " 55 mv./ μ .

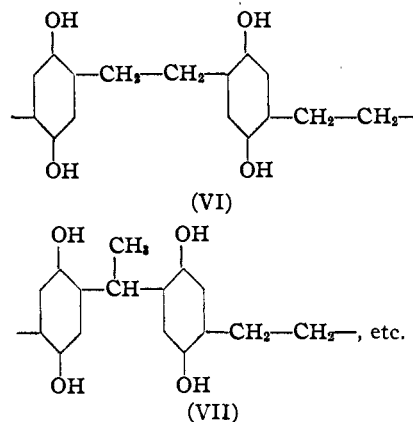
Discussion

It may appear odd that vinylhydroquinone should undergo polymerization readily when hydroquinone is an inhibitor for styrene polymerization. It was in fact found that vinylhydroquinone was somewhat more effective than hydroquinone itself in delaying the polymerization of styrene. This is in accord with the proposal of Cohen⁷ concerning the relative ease of oxidation of hydroquinones and their effectiveness as inhibitors of polymerization. Vinylhydroquinone is more readily oxidized than hydroquinone (see above) and hence would maintain a lower concentration of free radicals in any polymerization mixture.

Vinylhydroquinone itself, however, polymerizes quite rapidly. Perhaps the rate of chain propagation is greater than the rate at which free radicals are destroyed by oxidizing vinylhydroquinone to vinylquinone. An alternative explanation may be that the interaction of a free radical with an hydroxyl group of vinylhydroquinone does not lead to an inert product because the odd electron may migrate to the vinyl group where further chain growth may be initiated. Hence the type of chain-terminating reaction characteristic of hydroquinone merely leads to chain transfer in the case of vinylhydroquinone. On this supposition one might expect vinylhydroquinone to be a chain transfer agent in styrene polymerization rather than an inhibitor. The fact that it does inhibit styrene polymerization throws some doubt on the second of the explanations given above.

Some suppositions may be made regarding the structure of the polymer formed from vinylhydroquinone. It has been suggested⁸ that the very active *o*-hydrogens may become involved in the

reaction, leading to a certain amount of linking of the types VI and VII. This possibility has not been excluded. The following considerations make it seem that we may be dealing with a polyvinyl hydroquinone: (1) The substance appears to be polymeric:



The monomer is soluble in benzene, while even boiling benzene did not dissolve the polymer appreciably. (2) The substance has the physical appearance of polystyrene and is soluble in polar organic solvents. When this is combined with the observation that hydroquinone-formaldehyde polymers are dark in color and insoluble it would appear a reasonable conclusion that there is not much cross-linking of the types VI and VII present. The analogy is not strict, however, for phenols are known to polymerize with formaldehyde in part through $-OH$ interactions and this may account for the differences noted. (3) The majority of the $-OH$ groups in the polymer are free to be oxidized and reduced, as shown by the oxidation data. (4) The mid-point potential falls at a reasonable value between those of hydroquinone and ethylhydroquinone, and close to that of vinylhydroquinone. This is strong evidence that there is not much substitution on the rings such as would be suggested by the structures VI and VII and similar ones. At the suggestion of a Referee experienced in this field we have used the term polymerized vinylhydroquinone to describe the polymer rather than polyvinylhydroquinone until more concrete evidence can be brought to bear on the structure.

The increased slope and the shape of the oxidation curve of the polymer were interpreted in the previous paper¹ as possibly due to the accumulation of semiquinone during the titration. This interpretation was based on the appearance of a pink color near the beginning of the titration, its persistence during the titration, and its diminution toward the end-point, and the relation between color-formation, semiquinone formation and increased slope of the titration curve as worked out by Michaelis and his co-workers.⁹ A mechanism for the accumulation of semiquinone was suggested in the hampering of dismutation un-

(7) S. G. Cohen, *THIS JOURNAL*, **69**, 1057 (1947).

(8) By Mr. George W. Barber.

der the constraints put on the oxidizable residues by their being fastened on a long chain. It has seemed to us, also, that another phenomenon may contribute to the slope and shape of the titration curve of the polymerized vinylhydroquinone.

It may be assumed that the spatial arrangement of an oxidizable residue relative to other residues may affect its ease of oxidation through interactions such as might arise from hydrogen-bonding, dimerization, purely geometrical (steric) effects, as well as from actual differences in linkage such as were suggested in a previous paper.¹ If this were correct then it would follow that over these polymer chains there would be a spread of residues with different oxidizabilities, and during a titration the more easily oxidizable ones would go first (with the usual equilibrium restrictions), the more difficultly oxidizable ones requiring a higher potential. The titration curve would thus be "smeared out" over a wider potential range than for a single substance. To test this in a simple way a mixture of hydroquinone and ethylhydroquinone was titrated. The data obtained are shown in Fig. 3 in relation to the data for polymerized vinylhydroquinone. The slope of this curve ("δ") was about 0.055 v. per unit of μ . At no point during the titration was any color observed other than the pale yellow of the quinoid forms of the substances. A "statistical" effect such as this would complicate the interpretation of these curves. While we suspect that both the semiquinone formation and the statistical effect contribute to the total result we are not yet able to apportion to each its part. The correspondence of curves in Fig. 3 is probably fortuitous.⁹

The increased slope of the titration curve and the sequence of colors reported above for titrations of polymerized vinylhydroquinone in solution were observed also for the polymer dispersed in the presence of albumin. Another not unexpected observation was also made in these cases. With the dispersed polymer it was not possible to oxidize quite a number of the groups present. It seemed

(9) A Referee called our attention to a paper by Kern (W. Kern, *Z. physik. Chem.*, **A181**, 249 (1938)) on the titration of polyacrylic acids, where a spread of dissociabilities could be expected. The titration curve showed a slope different from that of isobutyric acid.

as though some of the groups, known to be present from in-solution oxidations of the resin, were unavailable when the resin was dispersed in a particulate form. The usual titration curves were obtained, however, when drawn on the basis of per cent. actually oxidized. When the resin was dispersed in the presence of a little albumin it seemed that more groups became available, though not all. In an experiment reported earlier¹ 77.8% were found in the presence of albumin, and upon reduction with hydrogen and retitration, 65% were reoxidizable. Some may have become unavailable due to conglomeration of the particles, or steric factors,¹ and some may have been destroyed by the oxidant. In another experiment with about 10 times as much albumin it seemed possible to titrate a larger percentage of the polymer groups, but the oxidation of albumin complicated matters. In a titration of the polymer (0.1863 me.) with bromine at a pH of 0.53 in the presence of 2.24 mg. of albumin (10 ml. solution) 86% of the groups could be titrated. Inaccessibility of certain groups to certain oxidizing agents might also affect the shape of the titration curve from an oxidant of one charge type or molecular size to another.

It will be interesting to determine the behavior of the polymer dispersed with polysaccharide and other natural and synthetic polymeric carriers. The stoichiometry of these combinations is also under investigation. It is further of interest to note that due to the constraints mentioned above the curves for the dispersed polymer are to a large extent linear, thus a normally logarithmic relationship has been converted to one substantially arithmetic.

Summary

Potentiometric titration curves are given for hydroquinone, ethylhydroquinone, vinylhydroquinone, and compared with the curve for polymerized vinylhydroquinone. Explanations are advanced for the differences observed, and the new features which appear in the titration of the electron exchange-polymer are discussed.

NEW HAVEN, CONN.

RECEIVED JUNE 26, 1948