[CONTRIBUTION NO. 1124, FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Electron Exchange Polymers. IV. Countercurrent Applications

BY HAROLD G. CASSIDY, MYER EZRIN AND IVOR H. UPDEGRAFF

RECEIVED SEPTEMBER 18, 1952

Polymers of vinylhydroquinone alone, with α-methylstyrene, and with styrene, cross-linked with divinylbenzene, may be used to effect reduction. The polymer becomes oxidized in the process and then becomes capable of acting as an oxidizing agent. This was shown by impregnating filter paper disks with polyvinylhydroquinone and applying the reagents using the technique of radial chromatography. It was also shown by preparing columns in which the copolymer with α-methylstyrene was supported on filter aid. Through these columns the solution of substance to be oxidized or reduced was percolated. The reversibility of the process was demonstrated. Some loss of activity occurred. It is suggested that these reductor or oxidizer columns have the advantage that they do not contaminate the reagent solutions except for the effect on the hydrogen ion concentration.

The previous paper[1] reported the preparation of high polymers of vinylhydroquinone alone and copolymers with styrene, α-methylstyrene, vinylpyridine and divinylbenzene, and described their properties and oxidation–reduction behavior in electrometric titrations.

This paper reports other ways of studying the oxidation behavior, namely, through countercurrent application in a chromatography tube, and in a "two-dimensional" system.

Experimental

Polymeric Materials ("Redox Resins").—These were prepared as described in the preceding paper.

Preparation of Exchanger.—*The linear polymers* must preferably be supported on a carrier which helps to make the reactive groups accessible. The polymer was dissolved in a minimum amount of solvent, 90% acetic acid being very convenient to use, then either of two courses could be taken. For qualitative work disks of smooth filter paper were soaked in the mixture and then dried in an evacuated desiccator containing vessels of concd. sulfuric acid and of sodium hydroxide pellets. The dried impregnated papers were either pink, or showed a tendency to become pink in time. For quantitative studies, highly purified filter-aid was mixed with the acetic acid solution to form a sludge. This was transferred to a relatively large amount of water, with vigorous mixing. The coated diatomaceous earth settled readily from a clear, or very faintly opalescent supernatant. The mixture was stirred and transferred to a chromatographic tube in which a layer of filter-aid, on a wad of glass wool supported by a perforated plate, was already present. The column produced in this way was evenly packed and flowed at a suitable rate. *Cross-linked polymer* was ground in an agate mortar with *ca.* 25 times its weight of filter-aid moistened with 90% acetic acid (to assist in breaking down any physical inter-group interactions) and to help keep the temperature down. This was transferred to a prepared column. Since grinding breaks down the structure of the filter aid it might be desirable to mix in fresh filter-aid before the mixture is placed in the chromatography tube.

For purposes of control, hydroquinone was treated in the same way as the polymer.

Chromatography Tubes.—The type designed by Nestler[2] was particularly useful for quantitative work because all the liquid below the column could be removed for analysis by squeezing the rubber bulb on the lower tubulature (Fig. 1). For work in an inert atmosphere nitrogen can be led in through both tubulatures.

Experiments with Paper Disks.—As an example of the preparation of impregnated disks, polyvinylhydroquinone, 46 mg. (0.675 meq.) was dissolved in *ca.* 1.5 ml. of 90% acetic acid. In this were soaked 4–5.5 cm. disks of Whatman No. 1 filter paper. About $^3/_4$ of the mixture was taken up. Thus each disk contained about 0.12 meq. of polymer, or *ca.* 0.006 meq./sq. cm.

A dry disk was placed between two flat pieces of glass, the upper piece having a small hole at the center through which reagents could be introduced.[3] A solution introduced through this hole spread out radially in the paper as a disk. The glass plates of this filter paper sandwich gave some protection from the air. To examine the paper the upper glass plate was removed and the paper spotted, or streaked from a point near the center outward with test reagent (the brush method of Zechmeister[4]).

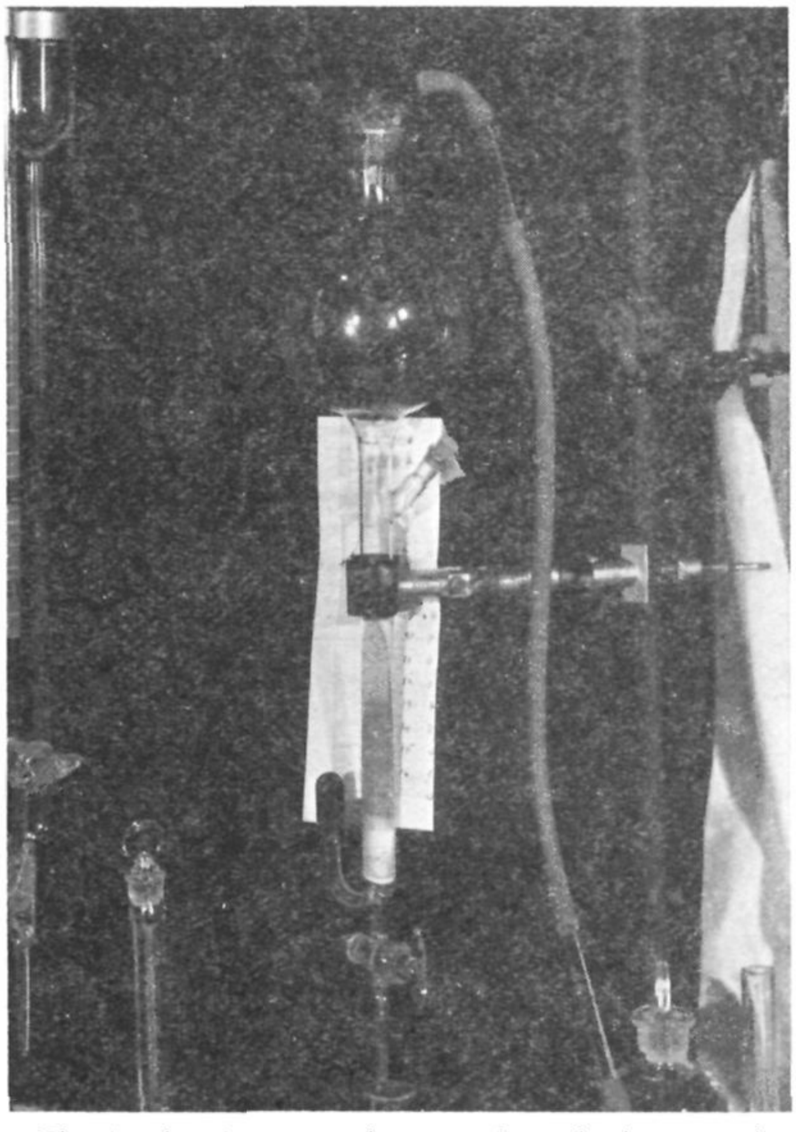

Fig. 1.—An electron exchanger column is shown resting on a white column of filter-aid. The exchanger is reducing a dichromate solution, and a brown oxidized zone can be seen to extend half-way down the short exchanger column. To quantitatively remove the liquid below the column the rubber bulb on the lower tubulature is squeezed. Reagents can be introduced through the upper tubulature, or at the top of the reservoir bulb. The arrangement shown at the top of the bulb permits pressure to be applied. We are indebted to Mr. Karl J. Sax for the photograph.

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[1] M. Ezrin, I. H. Updegraff and H. G. Cassidy, THIS JOURNAL, **75**, 1610 (1953).

[2] F. H. M. Nestler and H. G. Cassidy, *ibid.*, **72**, 680 (1950).

[3] W. G. Brown, *Nature*, **143**, 377 (1939).

[4] L. Zechmeister, L. Cholnoky and E. Ujhelyi, *Bull. soc. chim. biol.*, **18**, 1885 (1936).

a.—A few drops of aqueous ferric chloride, about 0.05 *N* (*ca.* 0.01 meq.) were run into the paper. An orange zone of oxidized polymer formed. A few drops of *N* sulfuric acid washed the reagent out of this zone. When the top plate was removed and the paper was streaked with reagents clear evidence of reduction of substantially all the ferric ion to ferrous was obtained: ferricyanide gave Turnbull blue: ferrocyanide gave a pale blue streak which intensified on standing in the air: α-nitroso-β-naphthol gave a green color. Untreated filter paper showed no reduction of ferric ion under the same conditions of test. The experiment was repeated many times, and in addition to the above test reagents α,α'-dipyridyl was used, giving a scarlet red with the ferrous ion.

b.—Fresh ferricyanide solution in a *p*H 6.6 phosphate buffer was introduced into a paper. A pink zone 3 cm. in diameter was formed. This was washed with buffer until its diameter was 6 cm. The outer edge of the wet area was yellow, the zone of reagent being washed to the periphery. Tests with various reagents showed reduction of ferricyanide to ferrocyanide; silver nitrate gave a brown color at the outside edge of the zone, and was reduced, the color being yellow in the central zone from which the ferrocyanide has been washed: a ferric chloride streak became progressively more intense blue from the central part of the wet area outward, and the peripheral zone gave prussian blue; cupric ion gave brown at the periphery, remaining blue over the inner portion of the wet area; ferrous ion gave a blue color at the periphery.

c.—The reversible nature of the reaction was demonstrated repeatedly with different papers by means of the following experiment. A small drop of iodine in potassium iodide solution at *p*H 6.4 or *p*H 7 was placed onto the paper. A brownish-black zone formed. When more of the pure buffer was introduced the zone broadened and the color disappeared as the iodine was reduced by the polymer. At this point if the top plate was removed no test for free iodine could be obtained (starch–KI). All the iodine had been reduced to iodide. In another experiment the iodine solution was introduced, and then the iodide was washed out of the central zone of oxidized polymer with more of the nearly neutral buffer. At this point, *N* sulfuric acid was introduced. No reaction occurred. However, on introducing a drop of dilute potassium iodide solution in *N* sulfuric acid, the iodide was immediately oxidized to brown iodine by the oxidized polymer. This was confirmed by a strong blue starch test. Thus, the polymer can be oxidized by iodine in potassium iodide in neutral solution, and this oxidized polymer, which remains *in situ* in the paper, can then oxidize iodide to iodine in acid solution.

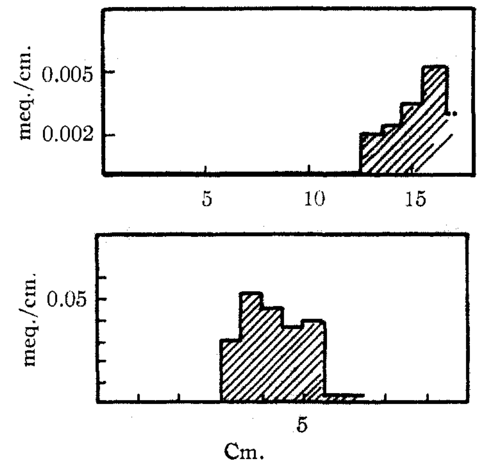

Fig. 2.—Break-through profiles are shown for a reducing and an oxidizing cycle. Instead of measuring volume collected, it was more convenient to measure the change in height of the liquid column above the exchanger. On the *x*-axis is plotted the effluent in terms of the height of column (20 ml. of reagent, washed into the tube with a little water, gave a column 16.5 cm. high). On the *y*-axis is the milliequivalents collected divided by the length of the column which passed into the receiver. No correction was made for the interstitial liquid in the column at the beginning of the experiment. The profiles merely show the shape of the zone in terms of concentration. In the upper figure the reduced column is reducing iodine in KI. The iodine finally broke through at *ca.* 10.6 cm., the first fraction collected extending to 12.5 cm. In the lower figure the oxidized column is oxidizing iodide under acid conditions and the curve shows the breaking through of a zone of iodine which was produced.

When papers were impregnated with hydroquinone in the same way, the behaviors were very much the same in experiments of the types a to c. The small amounts of liquid needed to move reagents along the paper were apparently insufficient to displace the hydroquinone very much.

Experiments with Columns.—Vinylhydroquinone–α-methylstyrene copolymer (14.945 mg.) a light, fluffy, faintly pink substance, was dissolved in 3 ml. of 90% acetic acid. A few flecks remained undissolved; 250 mg. of filter-aid which had been exhaustively extracted with petroleum ether, dried, and ignited, was mixed to form a slurry which was poured into 30 ml. of water, with vigorous stirring. A flocculent, pale pink mass settled out, leaving the supernatant clear, with a very faint opalescence. The material in a narrow tube flowed too slowly, so it was mixed with 250 mg. more of the filter-aid, and poured as a slurry into a wider chromatography tube already containing 0.5 g. of the filter-aid. The column was 1.5 cm. high × 1.3 cm. and rested on a filter-aid column of the same dimensions. There was no evidence, on washing the column, that any of the polymer passed out; there was no reducing action present. The column stood overnight bathed in KI–HCl solution (reducing conditions) and was a pale pink in color.

The following protocol illustrates the behavior of the column, which by calculation on the basis of a 1:1 ratio copolymer contained 0.117 meq. of oxidation–reduction capacity. The flow rate, when unaided by applied pressure, was *ca.* 5 ml./30 min.

a.—The column was washed with 1 ml. of water, then 1 ml. of *p*H 7.8 phosphate buffer, then treated with a mixture of 10 ml. of 0.0155 *N* iodine in KI and 10 ml. of buffer. The liquid column extended 16.5 cm. above the exchanger. As it flowed in a dark zone gradually formed extending from the top of the exchanger downwards. The yellow iodine color "broke-through" after about $^2/_3$ of the liquid had passed through the column, indicating that iodine had been reduced. The break-through pattern, in terms of length of liquid column rather than actual volumes, is shown in Fig. 2. The column was now light tan in color, with a narrow pale tan top layer. Washing with 1 + 5 + 3 ml. buffer removed excess iodine; 1 ml. of water brought out no more. Iodine reduced (sum of 7 fractions) was 0.122 meq.

b.—The column was now treated with a mixture of 5 ml. of 5% KI with 5 ml. of 8 *N* HCl. There was an immediate oxidation of iodide by the column and an intensely brown zone formed. This moved down the column, with a width of *ca.* 3 mm. at the foot. Some tailing was evident. The column, after no more iodine was formed (washed with 1 ml. of water then 9 ml. of 0.1 *N* hydrochloric acid) was almost white, except for a buff-colored 2 mm. layer at the top. The break-through pattern is shown in Fig. 2. Iodine produced (sum of 8 fractions) was 0.117 meq.

c.—The column was now put through the same cycle again, washed with 1 then 4 ml. of *p*H 7.8 buffer, treated with 10 ml. of iodine solution in 10 ml. of buffer. Iodine broke through somewhat earlier (channelling in column?). After all the solution had passed and the column had been washed with 1 + 5 + 3 ml. of buffer it was brownish-tan in color, with a very thin pale tan top layer. Iodine reduced (sum of 6 fractions) was 0.105 meq. This means that the column probably was not saturated with reagent and is consistent with the early break-through.

d.—The column was treated with 5 ml. of KI mixed with 3 ml. of 8 *N* HCl. This solution is still probably too acid for best results since a *trace* of iodine is set free spontaneously. The usual dark brown iodine zone appeared and moved down and out of the column. Total iodine produced was 0.098 meq. This seemed to be a good check with the oxidation state of the column in c.

e.—The column was now washed with 20 ml. of 0.1 *N* hydrochloric acid to remove all traces of iodine and iodide.

The last 2-ml. effluent gave no blue with starch solution and none after addition of potassium iodate. The column was then treated with 10 ml. of 0.0179 *N* potassium dichromate solution to which was added 2 ml. of 8 *N* HCl. A narrow brown zone *ca.* 2 mm. wide formed at the top of the column and moved down and out, leaving a light-yellow column. The effluent showed no color until about half the liquid had passed in, when a greenish cast (Cr^{++}?) was visible in it. Yellow dichromate began to break through at about this time. A sample taken contained no iodide. The column was now in the oxidized condition, and was washed with 5 + 5 ml. of 0.1 *N* hydrochloric acid, when in the last few ml. only a trace of dichromate (no blue starch test until KI was added) was present. The column reduced 0.106 meq. of dichromate.

f.—Another reduction with KI and hydrochloric acid produced the typical deep brown 3 mm. zone, and produced 0.122 meq. iodine.

g.—The column now remained under acid KI for *ca.* 2.5 days. It was pale tan in color. By error the column was not washed until no iodide was released by actual test. It was treated with acid dichromate (0.0179 *N* solution in an equal volume of 0.1 *N* HCl), of which 0.153 meq. was reduced. The collected effluent before determination of dichromate gave no test for iodine or iodide. No explanation for the high value is available except that the dichromate in the effluent was determined in a larger volume than previously (55 ml. instead of 35) and the solution may not have been made sufficiently acid to determine all the dichromate by the iodometric method.

h.—The oxidized column (tan in color) was now treated with 136.0 mg. (0.347 meq.) of ferrous ammonium sulfate hexahydrate dissolved in 10 ml. of 0.1 *N* HCl. The effluent was collected directly in standard cerate (0.02415 *N*). Only 0.019 meq. of ferrous ion was oxidized.

i.—The column, with this slight degree of reduction, showed no detectable reducing action on a solution of 0.0537 *N* ferric ion in an equal volume of 5.5 *N* HCl.

j.—After all the ferric ion had been washed from the column (5 + 5 ml. of 0.1 *N* HCl; no test for ferric ion in last few ml.) it was treated with 10 ml. of 5% KI mixed with 10 ml. of 0.1 *N* HCl. A zone of iodine formed and was washed out. When no more iodine appeared, the iodine produced amounted to 0.019 meq. The column appeared to have lost some capacity. When treated with iodine in *p*H 7.8 buffer it used only 0.028 meq., and a recycle with acid KI produced 0.032 meq. of iodine.

An exchanger column was prepared in the manner described above from 19.115 mg. of vinylhydroquinone–styrene–divinylbenzene cross-linked polymer. When the brownish exchanger was treated with acid KI a small amount of iodine (0.0015 meq.) was produced, confirming the supposition[1] that some oxidation occurs during preparation. When a mixture of 10 ml. of 0.0153 *N* iodine solution in 10 ml. of *p*H 7.8 buffer was passed through the column very slowly, a dark zone formed. After passage of the iodine, and washing until no more iodine or iodide appeared the column had reduced 0.127 meq. The amount of polymer taken was equivalent to 0.159 meq. calculated on the basis of 1:1 monomer, ignoring a small amount of divinylbenzene. About 80% of the groups were available. This experiment lasted 2 hours. When the column was treated with acid KI, using slight pressure to accelerate the flow about 10-fold (estimated) the efficiency of the column was much lowered, for only 0.019 meq. of iodine was produced.

A column made up under the same conditions as the first with hydroquinone showed the expected behavior. Hydroquinone, 15.65 mg. (0.284 meq.), was used. The hydroquinone leached out of the column to the extent that when the column was treated with iodine at *p*H 7.8, as above, there was reduction to the extent of only 0.005 meq., and subsequent tests for quinone in the column by passage of acid KI indicated only a trace of the order of 0.001 meq.

Discussion

In 1906, Tswett[5] suggested that the chromatographic method might utilize not only adsorption interactions but processes involving chemical reactions such as oxidation. This paper has reported such an application. The analogy to adsorption chromatography while interesting is not exact, and it is hoped to discuss this aspect of the experimental work at a later date.

Two features of electron exchangers which are of considerable interest need to be pointed out. The first has to do with the differences expected in the use of these substances in batchwise and in countercurrent applications. The subject has already been discussed in general, and in connection with ion-exchangers.[6] In batchwise applications these substances would be useful for *poising* a system at a given potential. This is quite analogous to the use of an ion exchange-resin to adjust the concentration of a solution in anions or cations, or of an acid or alkaline resin for *buffering* a system at a given value.

In the countercurrent application, since the reagent solution moves against the fixed body of resin the oxidation or reduction should occur in a very effective manner. This chromatographic application might resemble in its superiority to the ordinary batchwise reaction the superior efficiency of chromatographic adsorption over batchwise adsorption.[6] This application does not appear to be of the sort studied by Knox and Thomas[7] in their investigation of the Jones reductor as a model for the kinetics of chromatography.

Related to this feature is a second. While at first sight these columns might be considered as organic analogs of the Jones reductor, they differ in an important respect. With properly insoluble polymers (such as were used in the experiments reported) the reductor (or oxidizer) *does not contaminate the solution* except that in acting as a reducer the column contributes protons to the solution (and an equivalent amount of electrons, of course), while in the oxidizing step the protons and electrons are abstracted.

The fact that protons enter the reaction makes it possible to adjust the oxidizing or reducing efficiency of the polymers by adjusting the hydrogen ion concentration. Thus there is available a method for adjusting the potential in these heterogeneous systems which depends on *mass-action* effects. A *chemical* method is presumably also available in the ability to change the potential range by appropriate substitution on the quinoid nucleus, or by the use of other oxidation–reduction groups.

A final point which may be mentioned is that should these oxidation–reduction groups participate in ion exchange either through the usual coulomb interactions or through chelation, then a resin which in the reduced form retained a cation, say, could, on being oxidized become no longer an ion exchanger, and thus manifest a self-purging property.

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[5] M. Tswett, *Ber. Deut. Botan. Ges.*, **24**, 316 (1906).

[6] H. G. Cassidy, "Physical Methods of Organic Chemistry," A. Weissberger, ed., Vol. V, Interscience Publishers, New York, N. Y., 1951, Chapter VI and p. 286.

[7] K. Knox and H. C. Thomas, *J. Chem. Phys.*, **19**, 224 (1951).