pressions relating microscopic and macroscopic equilibrium constants.

The author is indebted to Professor John T. Edsall for his very helpful suggestions.

Summary

General expressions are derived relating microscopic and macroscopic equilibrium constants of ampholytes (equations 5 and 6). The concentration of any microscopic ion is given in terms of microscopic equilibrium constants, the hydrogen ion concentration and the total ampholyte concentration (equation 4).

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[CONTRIBUTION NO. 31 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

Systematic Studies on Palladium-Synthetic High Polymer Catalysts

BY KEVIN E. KAVANAGH[1] AND F. F. NORD

In preceding investigations some applications[2,3] and morphological[4] properties of certain synthetic high polymer-noble metal catalysts, which are highly effective and stable at ordinary pressure and room temperature as well as in acid, neutral and alkaline media, were established. On the basis of their structure as derived from X-ray patterns, it appears to be, however, unpredictable whether *e. g.* PVA, a long chain poly-hydroxy linear polymer,[5] or its derivatives would be preferable in some hydrogenations. It must also be borne in mind that PVA crystallizes readily, whereas polyvinyl acetate (PVAc) exhibits an amorphous pattern, as gum arabic (GA) probably does.

Accordingly, and upon consideration of the reduction of palladium chloride to metallic palladium by means of PVA, it was thought desirable to ascertain whether PVAc and related acetals, in which the acetyl group of PVAc is replaced to varying extent by different aldehydes, may serve as colloidal carriers. Moreover, the fact that the solubility conditions of these products are distinctly different from those of PVA, gave rise to a systematic study of the functioning of these microheterogeneous and multiphase systems in catalytic hydrogenations.

In view of the favorable results recorded in the hydrogenation of cystine,[6] an investigation of the quantitative influence of catalyst poisons, such as thiophene, was undertaken also.

Experimental

Purification of Materials

Dioxane.—U. S. P. dioxane[7] was boiled under a reflux condenser for seven hours with 10% of *N* hydrochloric acid to decompose the ethylene acetal present as an impurity, while a slow stream of nitrogen was bubbled simultaneously through the liquid to remove the acetaldehyde formed. The purification of other solvents and acceptors was described previously.

Preparation of PVAc-Pd Catalyst.—When alcohol is the solvent used: 125 mg. of PVAc is weighed out and to it is added a volume of absolute ethyl alcohol and then a volume of water which will bring the total volume up to 50 cc., including 1 cc. of $PdCl_2$ which contains the 10 mg. of Pd. Thus, the volumes of alcohol and water added will vary inversely. As will be pointed out later, there is a definite optimum water concentration. The solution of the PVAc in the alcohol-water mixture, which does not reduce $PdCl_2$, will take some time, approximately two hours. However, the preparation of a more concentrated PVAc-alcohol solution, from which less concentrated solutions could be made, is impractical, because PVAc is not very soluble in absolute alcohol, being more soluble in 95% alcohol. Even in this latter medium it is not too soluble, its limit of solubility being about 125 mg. per 50 cc., *i. e.*, 0.25%.

When acetone is the solvent, two procedures are possible. The PVAc may be weighed out for each individual sample of catalyst and then varying quantities of acetone and water added as in the experiments using alcohol as a solvent. The dispersion of the PVAc in acetone is much more rapid than in alcohol. On the other hand, because of the considerable solubility of PVAc in absolute acetone, a 2% solution of PVAc in absolute acetone may be prepared and then from this a volume may be taken which will give the desired amount of polymer. To this are then added varying quantities of absolute acetone and water to give a volume of 49 cc.; the 50th cc. is the 1 cc. of $PdCl_2$ containing the 10 mg. of Pd.

The catalysts thus prepared by either of the above methods, are introduced into the shaking vessel, reduced by hydrogen for five minutes and the rate of hydrogenation measured after introduction of the acceptor. Because of the limited solubility in alcohol, 125 mg. of PVAc was invariably taken when this solvent was used. A wider latitude in concentration is possible when acetone is the solvent.

Determination of Rates of Hydrogenations.—In Fig. 1, the velocities of PVAc-Pd catalysts dissolved in alcohol with varying concentrations of water, are plotted; 1 cc. of nitrobenzene is the substrate in all these cases. Curve A, representing a catalyst with but 1 cc. of water present, which was the volume of the aqueous $PdCl_2$ solution added, shows a much slower velocity of hydrogen transfer than the other catalysts in which the volume of water present is increased from 1 cc. to 3 cc., then to 5, and to 7 cc. The colloidal Pd solution produced on reduction of the PVA-$PdCl_2$ is very unstable when only 1 cc. of water is present and the Pd particles aggregate after about five minutes of use. When the volume of water is increased to 3 cc., the tendency to flocculate is nullified and a stable colloid is obtained. From curve B it can be seen that the preparation containing 3 cc. of water produces an excellent hydrogena-

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(1) Abridged from a part of the dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate Faculty of Fordham University, 1943.

(2, 3) Louis D. Rampino and F. F. Nord, THIS JOURNAL, **63**, 2745, 3268 (1941); **65**, 429 (1943); M. S. Kulpinski and F. F. Nord, *J. Org. Chem.*, **8**, 263 (1943).

(4) Louis D. Rampino, Kevin E. Kavanagh and F. F. Nord, *Proc. Nat. Acad. Sci. U. S.*, **29**, 246 (1943).

(5) E. Dammann, F. E. M. Lange, M. A. Bredig and F. F. Nord, *Biochem. Z.*, **288**, 421 (1936); C. S. Fuller, *Chem. Rev.*, **26**, 163 (1940); R. C. L. Mooney, THIS JOURNAL, **63**, 2828 (1941).

(6) Kevin E. Kavanagh, *ibid.*, **64**, 2721 (1942).

(7) A. Weissberger and E. Proskauer, "Organic Solvents," Clarendon Press, Oxford, 1935, p. 140.

tion rate. The efficiency of the catalysts decreases slightly when the volume of water is increased to 5 and 7 cc. This diminution in activity increases as the volume of water present is increased from 3 cc. Curves C and D represent catalysts containing 5 cc. and 7 cc. of water, respectively. Curve E shows the hydrogenation rate of an alcoholic PVAc–Pd catalyst containing 3 cc. of water, of which one-half cc. was 4% sodium carbonate, used to neutralize the hydrochloric acid formed by the reduction of the $PdCl_2$. This addition of sodium carbonate renders the catalyst slightly alkaline. The catalyst becomes more efficient in alkaline medium, as may be seen from this curve.

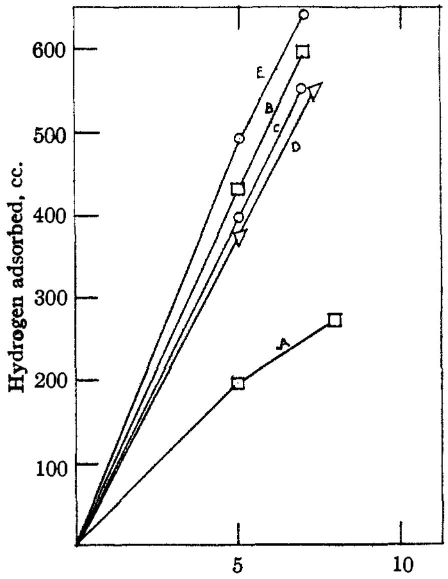


Fig. 1.—PVAc–Pd in ethanol: substrate, 10 mg. Pd, 125 mg. PVAc (GV-15); acceptor, 1 cc. of $C_6H_5NO_2$; A, 49 cc. EtOH, 1 cc. H_2O; B, 47 cc. EtOH, 3 cc. H_2O; C, 45 cc. EtOH, 5 cc. H_2O; D, 43 cc. EtOH, 7 cc. H_2O; E, 47 cc. EtOH, 2.5 cc. H_2O, 0.5 cc. 4% Na_2CO_3. All measurements are converted to 25° and 760 mm.

The maximum activity is exhibited by an alcoholic PVAc–Pd catalyst containing 3 cc. of water. It was believed at first that the ready coagulation of the catalyst, in which there was only 1 cc. of water, was due to the poorer solubility of the PVAc in absolute alcohol than in 95% alcohol. However, the necessity of a certain percentage of water, also observed with catalysts in which the PVAc was dissolved in acetone, in which it is quite soluble, and also when other polymers were used, as described later, suggested that it was more than a solubility effect. However, the decrease in activity when the concentration of water is increased above 3 cc. can be explained by the fact that the increasing water concentration tends to flocculate the PVAc–Pd.

Figure 2 shows the hydrogenation rates of PVAc–Pd catalysts in acetone with varying concentrations of water per 50 cc. of solution. As shown by Curve A, the rate is negligible and the colloidal catalyst coagulated quickly when only 1 cc. of water was present. This tendency to flocculate was not overcome in this series until the water concentration reached 9 cc. (Curves B, C and D) when a stable colloid was obtained. There was not much difference in the efficiency of the catalyst containing 9 cc. (curve D) and 12 cc. (curve E) of water. At these concentrations, the maximum efficiency was attained, for a decrease is noted when the volume of water is increased to 15 cc. (curve F). All these catalysts, whose hydrogenation velocities are graphed, contain 300 mg. of PVAc per 50 cc. of catalyst; however, when the amount of PVAc present is increased to 500 mg., a very similar set of curves is obtained.

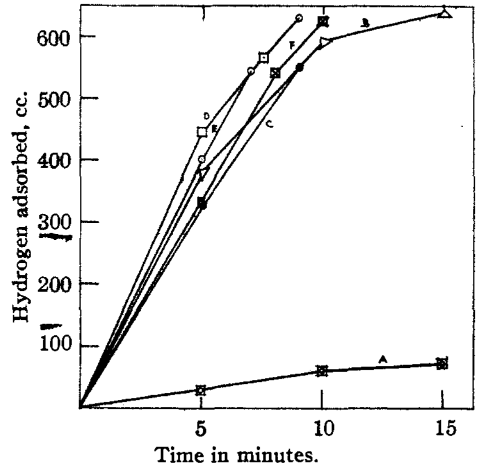


Fig. 2.—PVAc–Pd in acetone: substrate, 10 mg. Pd, 300 mg. PVAc (GV-15); acceptor, 1 cc. of $C_6H_5NO_2$; A, 49 cc. acetone, 1 cc. H_2O; B, 47 cc. acetone, 3 cc. H_2O; C, 44 cc. acetone, 6 cc. H_2O; D, 41 cc. acetone, 9 cc. H_2O; E, 38 cc. acetone, 12 cc. H_2O; F, 35 cc. acetone, 15 cc. H_2O. All measurements are converted to 25° and 760 mm.

All these curves, both in alcohol and acetone, were obtained by using Gelva V-15 PVAc. The V-15 represents the viscosity in centipoises, determined at 20°, of a benzene solution containing 86 mg of this Gelva per liter. Various other grades of PVAc, both Gelva (Shawinigan) and RH (du Pont) products, were obtained and their efficiency as colloidal carriers for metallic Pd tested. In the Shawinigan group, the number following the trade name, Gelva, is the viscosity expressed in centipoises; in the du Pont group, the number following does not indicate the viscosity but is merely a serial number. Therefore, the viscosity in centipoises is included in parentheses each time a du Pont grade is referred to. The viscosity is a convenient means of distinguishing one grade from another for it is also a measure of the degree of polymerization of the PVAc.

Some striking results were obtained when PVAc of different degrees of polymerization was used to make PVAc–Pd catalysts and their hydrogenation rates were measured. The various grades of PVAc whose efficiencies as colloidal carriers were determined, were as follows: Gelva V-15, Gelva V-60, RH-361 (650–800), RH 407 (55–70), RH 410 (4–6). Arranging these in the order of the size of the macromolecules, RH 410 (4–6) has the smallest particle size; Gelva V-15 is next; the Gelva V-60 and RH 407 (55–70) can be grouped together because of their similarity in viscosity and particle size; finally RH 361 (650–800) has an extremely large particle size, as is evidenced by its very great viscosity.

The efficiency of these different grades of PVAc, with their varying size of macromolecules, as colloidal carriers for metallic Pd is measured by noting the rate at which Pd, supported by different grades of PVAc, transferred hydrogen in the reduction of nitrobenzene (Fig. 3).

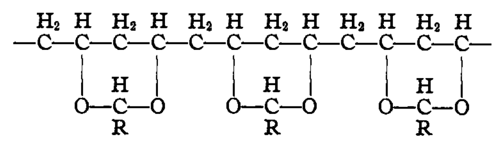
The rather poor catalyst formed with a PVAc of low polymerization, RH 410 (4–6), is shown in curve A. With PVAc of increased macromolecule size, Gelva V-15, the maximum efficiency is obtained (curve B). As the degree of polymerization increases in Gelva V-60 and RH 407 (55-70), the efficiency decreases slightly and, as would be expected from their viscosities, these two display very similar hydrogenation rates (curve C). When the macromolecules become very large, as in RH 361 (650–800), as evidenced by the high viscosity, there is a considerable drop in the effectiveness of the polymer as a colloidal carrier (curve D). All these experiments were performed with PVAc dissolved in ethyl alcohol. To reaffirm this finding a RH 361 (650–800) PVAc–Pd catalyst in acetone was prepared and compared with a Gelva V-15 PVAc–Pd catalyst of similar composition. Their rates of hydrogenation confirmed the previous results: for it was found that the RH 361 (650–800) PVAc–Pd catalyst (curve F), with its much greater degree of polymerization, is much less efficient than the Gelva V-15 PVAc–Pd catalyst (curve E). The difference is far more pronounced in acetone than it is in alcohol. To exclude the possibility that this polymer chain length effect is not just a result of differences in the optimum concentration value which may be different for the various grades of PVAc, a comparison was made of the efficiency of two PVAc–Pd catalysts in which the concentration of RH 361 (650–800) and Gelva V-15 was lowered to 100 mg. The catalyst which has 100 mg. of Gelva V-15 PVAc (curve G) is about twice as efficient as the catalyst which contains 100 mg. of RH 361 (650–800) PVAc (curve H). Both catalysts were dissolved in acetone.

Discussion

When the size of the polymer is too small, as in RH 410 (4–6), a poor colloidal carrier is obtained. However, when the degree of polymerization becomes too great, as in RH 361 (650–800), there is also a slackening in the efficiency of the polymer. This result, indicating an optimum size of macromolecule, may be due to a combination of peptizing and coating effects.[8] Rideal[9] found that there was an optimum concentration of GA in GA–Pd catalysts. Upon the presence of this optimum amount required for peptizing the metal, the addition of further quantities resulted in a diminution of activity due to a coating of the surface of metal with excess colloid. This optimum degree of polymerization may be a physical phenomenon whereby, when the macromolecules are too large, they prevent the ready adsorption and desorption of hydrogen which is necessary for efficient hydrogenation. It seems from these results that a certain size of molecule is necessary for efficient peptization but, when the molecule becomes too large, the beneficial peptizing effect is hindered by a coating effect.

PVAc in alcohol and acetone proved to be an excellent colloidal support for Pd in the reduction of nitrobenzene. A PVAc–Pd catalyst possessed a much higher rate of hydrogen transfer than did PVA–Pd in this hydrogenation and also in the reduction of other organic compounds. For example, benzaldehyde was reduced completely to toluene in fifty minutes by a PVAc–Pd (alcohol) catalyst, whereas it took a PVA–Pd catalyst five hours to accomplish this. This is partially a solvent effect, nitrobenzene and benzaldehyde being more readily soluble in 95% alcohol than in a 50% alcohol–water mixture.

Hydrogenations with PVA-Acetals as Carriers.—The encouraging results with PVAc led to an investigation of the feasibility of employing other synthetic high polymers as colloidal carriers for noble metals. For the extension of the investigation, Formvar (Fv), Butvar (Bv) and Alvar (Av), were chosen. These products are acetals of polyvinyl alcohol in which the alcohol is condensed with formaldehyde, butyraldehyde and acetaldehyde, respectively. They are produced by replacement of the acetyl group in PVAc resins by the various aldehydes. They are distinguished from one another by the viscosity of the Gelva (PVAc) resin from which they are derived and by the extent of this replacement, *e. g.*, Formvar 15–95 is made from Gelva 15 by replacing 95% of the acetyl radicals. Av 15–70 and Bv 25–98 were the grades of these polymers used. The structure of this type of compound can be seen from this representative formula



R is either an alkyl group or a H atom.

These acetals of PVA were soluble in glacial acetic acid and dioxane. It was found that all of these polymers can be used as colloidal carriers for a Pd catalyst. Av–Pd is the least efficient of the three catalysts, while Fv–Pd is the best, approximating in reducing efficiency PVA–Pd catalysts when nitrobenzene is used as an acceptor.

With dioxane as a solvent, Av does not prove to be a good carrier for Pd. Av–Pd catalysts in dioxane, containing 10 mg. of Pd and with 1 cc. of nitrobenzene as an acceptor, transfer only 40 cc. of hydrogen in a five minute period and this at the most favorable Av concentration, *viz.*, 250 mg. per 50 cc. of solution. This does not compare

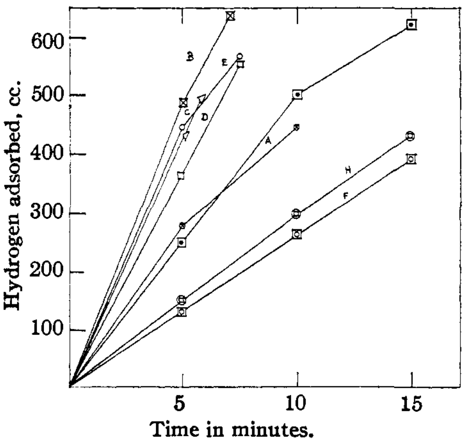


Fig. 3.—Effect of polymer chain length: acceptor, 1 cc. of $C_6H_5NO_2$; substrate, 10 mg. Pd, 125 mg. PVAc in 47 cc. EtOH, 2.5 cc. H_2O, 0.5 cc. of 4% Na_2CO_3: A, RH 410 (4–6); B, GV-15; C, GV-60 and RH 407 (55–70); D, RH 361 (650–800). Substrate, 10 mg. Pd, in 41 cc. acetone, 9 cc. H_2O: E, 300 mg. PVAc-GV-15; F, 300 mg. PVAc-RH 361 (650–800); G, 100 mg. PVAc-GV-15; H, 100 mg. PVAc-RH 361 (650–800). All measurements are converted to 25° and 760 mm.

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[8] T. Iredale, *J. Chem. Soc.*, **119**, 109 (1921).

[9] E. K. Rideal, THIS JOURNAL, **42**, 749 (1920).

favorably with the 225 cc. and 450 cc. adsorption of PVA and PVAc, respectively. An interesting fact noted, however, is that for the attainment of this maximum, a certain amount of water is necessary, specifically 3 cc. This behavior is analogous to the observation reported under the PVAc catalysts.

Bv–Pd and Fv–Pd in dioxane were not particularly good hydrogenation catalysts either. Bv–Pd was a slightly better catalyst than Av–Pd; Fv–Pd was the best of the three by a wide margin.

These acetal polymers do not form with Pd efficient colloidal hydrogenation catalysts in dioxane. However, when dissolved in acetic acid, colloidal Pd catalysts, capable of a much higher rate of hydrogen transfer, were obtained. The same order of efficiency as in dioxane prevails; Fv is the best colloidal carrier while Av is the poorest.

Figure 4 shows the hydrogenation rates toward 1 cc. of nitrobenzene which are obtained when acetal–Pd catalysts dissolved in acetic acid are used. The catalysts in acetic acid are prepared in the same manner as they were prepared in dioxane, and here the constancy of the rate of hydrogenation is striking.

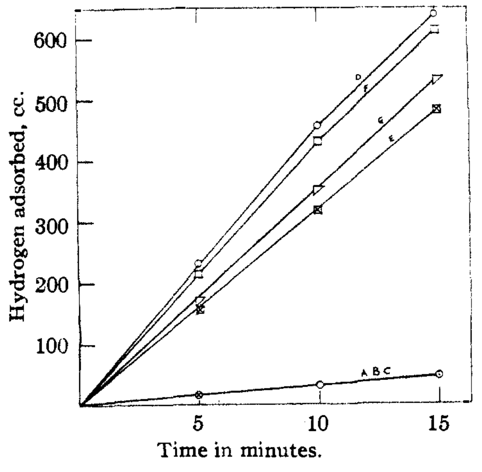

Fig. 4.—Av–, Bv–, Fv–Pd in acetic acid: substrate, 10 mg. Pd; acceptor, 1 cc. of $C_6H_5NO_2$: A, 250 mg. Fv, 49 cc. acetic acid, 1 cc. of H_2O; B, 250 mg. Bv, 49 cc. Aa, 1 cc. of H_2O; C, 250 mg. Av, 49 cc. Aa, 1 cc. of H_2O; D, 250 mg. Fv, 44 cc. Aa, 6 cc. of H_2O; E, 250 mg. Fv, 41 cc. Aa, 9 cc. of H_2O; F, 250 mg. Bv, 44 cc. Aa, 6 cc. of H_2O; G, 250 mg. Av, 44 cc. Aa, 6 cc. of H_2O. All measurements are converted to 25° and 760 mm.

Curve ABC in Fig. 4 shows the hydrogenation efficiency of the three catalysts, Fv–Pd, Bv–Pd, and Av–Pd in acetic acid when there is only 1 cc. of water per 50 cc. of solution present in each. Curve D is a Fv–Pd catalyst at optimum concentration of Fv, *viz.*, 250 mg., and optimum volume of water, *viz.*, 6 cc. A Fv–Pd catalyst with 250 mg. of Fv and 3 cc. of water, approximates this catalyst in activity, Curve D, and can be represented by the same curve. When the volume of water present is increased to 9 cc. there is a definite drop in activity, as seen in Curve E. When the concentration of Fv is increased to 500 mg. there is little change in activity and the same effect is shown, on varying the volume of water, as was shown in the samples containing 250 mg. of Fv. Curve F represents a Bv–Pd catalyst of optimum concentration of Bv (250 mg.) and water (6 cc.). When the volume of water is increased to 9 cc., a drop in efficiency takes place in a manner similar to that noted with Fv. Curve G shows a hydrogenation rate observed with an Av–Pd of optimum concentration of Av (250 mg.) and water (6 cc.). The fall in activity from Fv through Av is evident.

Discussion

The necessity of a certain quantity of water with all these organic solvent soluble polymers for the formation of an efficient catalyst is striking. It was noted with PVAc in both alcohol and acetone. The identical condition exists, as has just been shown, with the acetal polymers, Fv, Bv and Av. The amount of water necessary for the attainment of maximum efficiency varies from 3 cc. per 50 cc. of solution, in the case of PVAc in alcohol, to 9 cc. per 50 cc. of solution for PVAc in acetone. The percentage of water necessary seems to parallel the solubility of the polymer in the solvent. Thus, 3 cc. per 50 cc. is the optimum PVAc in alcohol in which the polymer is not very soluble, whereas 9 cc. per 50 cc. is the optimum for PVAc in acetone in which the PVAc is much more soluble. Unless a certain amount of water is present the colloidal suspension of the metal formed on reduction of the $PdCl_2$ is very unstable and coagulation occurs in a short time. The lack of activity of such preparations is undoubtedly the result of this coagulation. The presence of a certain percentage of water thus seems to be necessary for the formation of a stable colloidal suspension. This may be attributable to the fact that water is required to enable the polar substance present, hydrochloric acid or sodium carbonate, to ionize sufficiently to stabilize the lyophobic colloid, metallic Pd. Under this consideration, the lyophilic protective colloid, the organic-solvent-soluble polymer, PVAc, Fv, or whatever it may be, is unable to prevent the coagulation of metallic Pd particles unless there are enough ions present for the Pd particles to assume a zeta potential by absorbing a diffuse layer of negative ions and thus assist the colloid in preventing the coagulation.

Effect of Thiophene on the Hydrogenation Rate of Nitrobenzene.—The results obtained in the cystine hydrogenation[6] suggested that experiments be made to determine the relative effects of a catalyst poison on a PVA–Pd catalyst and on a Ga–Pd catalyst. As a consequence of the cystine hydrogenation and of the utilization[2] of the water gas reaction, for hydrogenation by Pd–PVA, it seemed that this catalyst was more impervious to poisons than were the older types. Thiophene had been found to be an effective poison for hydrogenation catalysts,[10] and accordingly this substance was used.

The effect on the hydrogenation rate of nitrobenzene by PVA–Pd and GA–Pd, caused by adding qualities of this poison, was used as a criterion of the resistance of these catalysts. A catalyst, containing 250 mg. of PVA and 20 mg. of Pd per 50 cc. of 50% alcohol solution, was prepared. One cc. of nitrobenzene was introduced into the vessel together with 0.02 cc. of thiophene. The hydrogen absorption data are plotted in Curve D, Fig. 5. The effect of the poison on the hydrogenation rate is easily discernible. This has fallen from about 250 cc. in a five-minute interval to about 20 cc. in the same period of time. The quantity of poison was then increased to 0.04 cc. The hydrogenation rate was further cut to about 12 cc. per five-minute interval (Curve C). GA catalysts were then prepared from 100 mg. of GA and 20 mg. of Pd per 50 cc. of 50% alcohol solution, and the poison added together with the 1 cc. of nitrobenzene, as in the PVA experiments. When the volume of thiophene was 0.02 cc. a transfer rate of 10 cc. per five-minute interval was obtained (curve B). Upon increasing this to 0.04 cc., a decrease in rate to about 5 cc. per five-minute interval was noted (curve A).

The superior protection exerted by the PVA is apparent. The PVA–Pd is about twice as efficient as GA–Pd in the presence of an equal volume of poison. From these experiments, it seems that the effect of the poison is directly proportional to the amount of poison added. As may be seen from Fig. 5, the doubling of the volume of poison results in a halving of the rate of transfer with both catalysts. If, as seems probable from the results previously obtained from adsorption measurements and from the electron micrograph data,[4] the particle size and surface area in GA–Pd and PVA–Pd catalysts are comparable, the superior resistance of the latter to poisoning is due to a quality factor. It is this quality factor, perhaps analogous to orientation, to which we previously attributed the superiority of the PVA–Pd over the GA–Pd. This quality factor may be the manner in which the PVA contributes to the peptization of the Pd particles, or it may be a more advantageous distribution of particles which is effected by the PVA. Whatever it is, it so influenced the surface of the hydrogenation catalyst that it became superior in performing its primary functions[11] of mutual adsorption of hydrogen and acceptor, combination of the two *in situ*, and desorption of the reduced compound. Thus it seems that two factors determine the efficiency of these catalysts, the particle size,[4] *i. e.*, the available surface, and a quality factor which differentiates one colloidal catalyst from another.

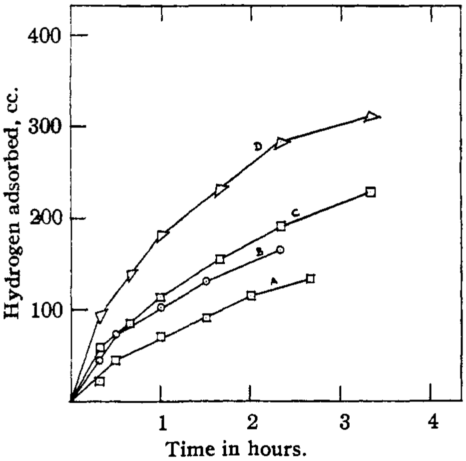

Fig. 5.—Effect of poison on PVA–Pd and GA–Pd catalysts: substrate, 20 mg. Pd in 50 cc. of 50% alcohol; acceptor, 1 cc. of $C_6H_5NO_2$: A, 100 mg. of GA, 0.04 cc. of thiophene; B, 100 mg. GA, 0.02 cc. of thiophene; C, 250 mg. of PVA, 0.04 cc. of thiophene; D, 250 mg. of PVA, 0.02 cc. of thiophene. All measurements are converted to 25° and 760 mm.

Acknowledgments.—This investigation was supported in part by a grant from the Penrose Fund of the American Philosophical Society and is being continued. The noble metal salts used were obtained by courtesy of Baker and Co., Inc., Newark, N. J., and the synthetic high polymers by courtesy of E. I. du Pont de Nemours, Inc., Wilmington, Del., and Shawinigan Chemicals, Ltd., New York, N. Y.

Summary

1. PVAc in alcohol or acetone was shown to be an effective colloidal support for palladium hydrogenation catalysts.

2. It was established that the degree of polymerization of a compound can be so high, which is to say that the particle size of a polymer can be so large, that a diminution in activity of the colloidal catalyst results.

3. The possibility of using various acetals of PVA, dissolved in acetic acid or dioxane as colloidal carriers for Pd catalysts was demonstrated.

4. The necessity of the presence of a certain percentage of water to assure stability and efficiency in these organic solvent soluble polymer catalysts was shown.

5. PVA–Pd has been shown to be a superior catalyst to GA–Pd in the presence of thiophene.

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(10) E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, 603 (1937).

(11) J. E. Nyrop, "The Catalytic Action of Surfaces," Ejnar Munksgaard, Copenhagen, 1937, 2nd edition, p. 9.