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Investigations on the Mechanism of Catalytic Hydrogenations.[1] XVI. Studies on Unsaturated Aliphatic Acids

BY W. P. DUNWORTH AND F. F. NORD

A kinetic study of the rate of hydrogenation of various unsaturated fatty acids has shown that at least three factors are important in determining the velocity of reduction, when colloidal Pd and Rh are employed as the catalysts in 70% ethyl alcohol solution. These are the degree of substitution of the double bond, the molecular weight of the compound and the position of the double bond. It has also been established that α,β-unsaturated acids hydrogenate most slowly with palladium while β,γ-unsaturated acids hydrogenate most slowly with rhodium.

Introduction

Previous work in this Laboratory has demonstrated the catalytic value of colloidal noble metals, supported by synthetic polymers.[2] A study of the mechanism of the catalytic hydrogenation of certain aliphatic compounds, particularly of the unsaturated aliphatic acids was therefore undertaken, employing both colloidal rhodium and palladium. These metals were chosen since it has been postulated[2] that they function by different mechanisms.

Experimental

The catalysts employed in this investigation were supported by polyvinyl alcohol. The Pd catalyst was used as Baker Colloid 46 of Baker and Co., Newark 5, N.J., and the Rh catalyst was prepared according to previous directions.[2] All the hydrogenations reported here were conducted with the same catalyst preparations. The Rh catalyst was particularly active. Acrylic and crotonic acids were commercially available preparations. The α,β-unsaturated five and six carbon acids were obtained by condensing the appropriate aldehyde with malonic acid, employing anhydrous pyridine containing 0.5% piperidine as a solvent.[3] Vinylacetic acid was obtained by hydrolyzing allyl cyanide with concentrated HCl.[4] The β,γ-unsaturated acids were obtained by condensing the appropriate aldehyde with malonic acid in the presence of anhydrous triethanolamine.[5] γ,δ-Pentenoic acid was obtained by condensing allyl bromide with sodium diethylmalonate, hydrolyzing the ester so obtained and decarboxylating the resulting acid.[6] γ,δ-Unsaturated hexenoic acid was obtained by condensing crotyl bromide with sodium diethylmalonate, hydrolyzing and decarboxylating.[7] The δ,ε-hexenoic acid was obtained by treating allylmagnesium bromide with formaldehyde converting the alcohol thus obtained to the corresponding bromide and running a malonic ester synthesis on the bromide.[8] The eight through twelve α,β-unsaturated acids were obtained by the method of B. Zaar[9] in which the appropriate aldehyde is condensed with malonic acid in the presence of anhydrous pyridine. The resulting product is considered to be a mixture of about 95% of the α,β-acid and 5% of the β,γ-isomer. The α,β-acid can be obtained pure by treating the mixture with about an equal weight of 85% sulfuric acid at 80° with stirring for six hours. By this procedure the β,γ-acid is converted to the γ-lactone which can be easily removed.

In all cases the starting materials for the preparation of the acids were carefully purified, and for the acids up to and including the six carbon acids the freezing point, the boiling point and the melting point of at least one derivative were utilized to check the purity of the individual acids. In the case of the higher acids the boiling point and neutral equivalent were employed to establish purity, since additional reliable data have not been recorded.

Hydrogenation of Organic Compounds.—In the case of the three to six carbon acids, generally samples of about 3 g. were used, while for the eight to twelve carbon acids five gram-samples were employed. It is known, however, that as long as an excess of unreacted substrate is present the rate of hydrogenation is virtually independent of the concentration of the substrate. In all cases 100 ml. of 70% ethyl alcohol was used as the solvent, 20 ml. of the colloidal catalyst (containing 10 mg. of either Pd or Rh) being employed in each hydrogenation. The hydrogenations were conducted in a special vessel which was designed for use with colloidal catalysts. Details of the vessel have been reported previously.[2] In other respects, the conditions of hydrogenation were similar to those reported in the following paper.

The results presented in this study were reproducible to about ±5%.

Discussion and Results

In Table I are recorded the values for the hydrogen uptake in ml./min. for the series three to six carbon acids, when Pd was used as the catalyst.

TABLE I

REDUCTION OF UNSATURATED ACIDS WITH COLLOIDAL Pd (HYDROGEN UPTAKE IN ML./MIN.)

No. of C atoms	α,β	β,γ	α,δ	δ,ε
3	145			
4	100	172		
5	73	115	210	
6	60	90	160	210

In Table II are recorded the values when Rh was employed.

TABLE II

REDUCTION OF UNSATURATED ACIDS WITH COLLOIDAL Rh (HYDROGEN UPTAKE IN ML./MIN.)

No. of C atoms	α,β	β,γ	γ,δ	δ,ε
3	90			
4	195	140		
5	175	125	210	
6	150	115	160	215

The rate of hydrogenation was found to be constant for all the hydrogenations reported except for the reduction of γ,δ- and δ,ε-hexenoic acid with Rh. In these cases, the values given in the tables are for the hydrogen uptake during the first minute of reduction. The actual values of hydrogen uptake in one series of experiments, for these acids in ml./min. are: γ,δ-hexenoic acid with Pd: 160, 140, 107, 88, 70, 40, 20 . . .; δ,ε-hexenoic acid with Pd:

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(1) Presented before the Symposium on Catalysts held at the Diamond Jubilee Meeting of the American Chemical Society, September, 1951. This and the following paper are abridged from parts of the dissertation of W. P. Dunworth, submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Ph.D., 1952.

(2) W. P. Dunworth and F. F. Nord, THIS JOURNAL, **72**, 4197 (1950), and previous articles in this series.

(3) A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2343 (1928).

(4) L. Falaise and R. Frongier, *Bull. soc. chim. Belg.*, **42**, 427 (1933).

(5) R. P. Linstead, *et al.*, *J. Chem. Soc.*, 740 (1931); 557 (1933).

(6) E. Schjanberg, *Ber.*, **70B**, 2385 (1937).

(7) E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 2153 (1929).

(8) R. P. Linstead and H. N. Rydon, *ibid.*, 1995 (1934).

(9) *Ber. Schimmel & Co., Akt. Ges.*, Jubilee Number, 299 (1929).

210, 180, 78, 57, 37, 25 . . .; δ,ϵ-hexenoic acid with Rh: 215, 245, 120.

At first it was suspected that traces of impurities might have been present but subsequent work could not establish the presence of any such impurities. As a further check, in each of the above mentioned cases the unsaturated acid, solvent and catalyst were shaken in the absence of hydrogen for one hour and then hydrogenated. The decrease in velocity was still observed. Farmer and Galley[10] have reported that when allyl alcohol is hydrogenated with hydrated platinum oxide a similar behavior is shown, except that toward the end of the hydrogenation the velocity rises sharply.

Since the velocity of hydrogenation seemed to vary with the molecular weight of the compound hydrogenated, the eight through twelve carbon α,β-unsaturated acids were then hydrogenated. The results are presented in Table III.

TABLE III

REDUCTION OF α,β-UNSATURATED ACIDS (HYDROGEN UPTAKE IN ML./MIN.)

No. of C atoms	Pd	Rh
8	144	203
9	121	180
10	113	150
11	123	165
12	95	138

To investigate further the effect of the molecular weight of a compound on its rate of hydrogenation various esters of acrylic and methacrylic acid were hydrogenated. The results of these observations are summarized in Table IV.

TABLE IV

REDUCTION OF UNSATURATED ESTERS (HYDROGEN UPTAKE IN ML./MIN.)

Alcohol portion of ester	Ph	Rh	Pd	Rh
	Acrylic acid ester		Methacrylic acid ester	
Methyl	150	125	100	100
Ethyl	170	140	115	110
n-Butyl	220	180	160	140
i-Butyl	210	170	...	...

It has been shown[11] that the degree of substitution of an olefin determines its rate of hydrogenation, unsubstituted olefins being hydrogenated most readily. Thus we should expect that terminally unsaturated fatty acids should hydrogenate more readily than their isomers. Our results, in general, are in accord with this statement. However, in the case of the hydrogenation of vinylacetic acid with Rh, this is not the case. In Table V are presented the values for the ionization constants for all the unsaturated fatty acids up to and including the six carbon acids.

TABLE V[12]

IONIZATION CONSTANTS OF VARIOUS UNSATURATED ACIDS ($K_t \times 10^5$)

No. of C atoms	α,β	β,γ	γ,δ	δ,ϵ
3	5.56			
4	2.03	4.48		
5	2.02	3.11	2.10	
6	1.98	3.05	1.91	1.90

A direct comparison of the ionization constant of the various acids with the rate at which they are hydrogenated by Rh (Table II) shows clearly that there is a remarkable relationship between these properties. Thus for isomeric acids with Rh as a catalyst it seems that the most important factor governing the rate of hydrogenation is the ionization constant, the higher its value the lower the rate of hydrogenation. This assumption was checked by hydrogenating α,β-octenoic acid in the presence of an equal weight of benzoic acid ($K_t \times 10^5 = 6.46$) with the Rh catalyst. The velocity of hydrogenation fell off considerably. Although the rate of hydrogenation of the various acids with the Rh catalyst is dependent upon the ionization constant of the acids, the degree of substitution of the carbon-carbon double bond also influences the rate. It is to be noted that the terminally unsaturated acids are monosubstituted olefins, while all the other unsaturated acids are disubstituted olefins. It has been shown[11] that disubstituted olefins hydrogenate more slowly than monosubstituted olefins. Thus although α,β- and γ,δ-pentenoic acids have very similar ionization constants, the former, a disubstituted olefin, is reduced at a lower rate than the latter, a monosubstituted olefin, with the Rh catalyst.

When palladium, however, is used as the catalyst the interaction between the carboxyl group and the ethylenic double bond appears to lower the rate of hydrogenation since unsaturated acids hydrogenate at lower rates than unsaturated acids in which the double bond is further removed from the carboxyl group.

Farmer and Galley[10] have reported that in the case of the hydrogenation of alpha, beta and gamma unsaturated hexenoic acid with hydrated platinum oxide the rate of hydrogenation increases with increasing distance of the double bond from the carboxyl group. They recorded hydrogenation velocities, which are very similar for the β- and γ-acids, but they re-used the same catalyst specimen, which may result in a decrease in effectiveness. In our work a significant difference was noted.

When equal weight mixtures of acids that hydrogenate at different rates were reduced, it was noted that the rate of hydrogenation of the mixture lay between the rates of the individual acids. The only exception was in the reduction of β,γ-acids with other acids, when rhodium was employed as the catalyst, in which case the rate fell to approximately that of the β,γ-acid. These results lead us to believe that there was no preferential reduction of one of the acids.

The most puzzling aspect of this study is that in the series of α,β-unsaturated acids, there is a gradual decrease in the rate of hydrogenation from the three carbon acids to the six carbon acids.

Hereafter there is a sudden large increase in the rate of hydrogenation of the eight carbon acid followed again by a gradual decrease. Since the bu-

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(10) E. H. Farmer and R. A. E. Galley, *J. Chem. Soc.*, 687 (1933).

(11) S. V. Lebedev, G. G. Kobliansky and A. O. Yakubchik, *ibid.*, **127**, 417 (1925).

(12) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1088 (1937); D. J. G. Ives, R. P. Linstead and H. L. Riley, *ibid.*, 561 (1933).

tyl esters of acrylic and methacrylic acid hydrogenate more rapidly than the corresponding methyl esters it seems unlikely that this effect could be due to a gradual decrease in solubility of the various acids. Moreover, decreasing solubility would not explain the abrupt change in the rate from the six to the eight carbon acids. There is a possibility that these variations may be due to steric factors which are dependent on the length of the carbon chain or possibly there may be some sort of micelle formation in the higher acids.

In order to further compare the Rh and Pd catalysts an attempt was made to hydrogenate various aliphatic nitro compounds. Both catalysts were ineffective for the reduction of nitromethane, nitroethane and 1-nitropropane. Rhodium but not palladium catalyzed the reduction of 2-nitropropane at a very slow rate. It thus appears that for Pd to function a higher electron density must be present for the unsaturated compound to be adsorbed by the catalyst. This assumption was checked by hydrogenating a mixture of 2-nitropropane and *n*-butyl acrylate with both palladium and rhodium. The addition of the nitro paraffin caused no variation in the rate of hydrogenation with Pd. With rhodium, however, the rate of hydrogenation was decreased by about 30% indicating that the 2-nitropropane is not absorbed by palladium.

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Investigations on the Mechanism of Catalytic Hydrogenations.[1] XVII. Reductions with Rhodium on Activated Carbon

BY W. P. DUNWORTH AND F. F. NORD

The reduction of various functional groups with a 5% rhodium on activated carbon catalyst has been investigated. This catalyst is useful for the reduction of the carbon–carbon double bond, activated nitro, carbonyl and nitrile groups, and quinones. It is also useful for the reduction of the various intermediates in the nitrobenzene to aniline system. A study of the rate of reduction of substituted nitrobenzenes to substituted anilines with this catalyst has shown that both the nature and position of the substituent alter the rate.

Introduction

Although noble metals have long been recognized as superior hydrogenation catalysts, little information is available regarding the catalytic properties of rhodium. It was reported,[2] however, that oriented rhodium films catalyze the hydrogenation of ethylene more rapidly than similar films of other metals. Previous work in this Laboratory[3] has also demonstrated that polyvinyl alcohol-supported colloidal rhodium and palladium possess strikingly different properties when applied as hydrogenation catalysts. To further study the catalytic properties of rhodium we have investigated the hydrogenation of various organic compounds with the aid of an activated carbon catalyst containing 5% of the metal.

Experimental

The organic compounds employed in this investigation were obtained in the following ways. Nitrobenzene, the substituted nitrobenzenes, azobenzene, azoxybenzene, crotonic acid, the quinones, ethyl cyanoacetate, benzonitrile, aniline, benzophenone, styrene and benzaldehyde were commercially available preparations of the highest purity. The nitroparaffins were obtained through the courtesy of the Commercial Solvents Corporation, hexaldehyde and diisobutyl ketone from Carbide and Carbon Chemical Corporation, and the acrylic esters from Rohm and Haas Company. Nitrosobenzene, hydrazobenzene and phenylhydroxylamine were synthesized in the laboratory. The various unsaturated acids: namely, α,β-hexenoic acid[4]; α,β-unsaturated eight-, ten- and twelve-carbon acids[5]; vinyl acetic acid[6]; β,γ-hexenoic acid[7]; γ,δ-pentenoic acid[8] and γ,δ-hexenoic acid[9] were also synthesized. The physical properties of all the compounds employed agreed with those reported in the literature. Five per cent. rhodium on activated carbon, lot #345 Baker & Company, was used for all experiments except for the reduction of quinones, the carbonyl group and the study of the concentration of the catalyst on the rate of hydrogenation of nitrobenzene. In these experiments lot #572 of the same catalyst was employed.

The hydrogenations reported here were carried out in a glass hydrogenation vessel at atmospheric pressure and room temperature.

The flask was shaken at a speed of 258 strokes/min. and the reaction followed volumetrically using water as the retaining liquid.

In each experiment 0.2000 g. of fresh catalyst was used. An initial study showed that if the catalyst was weighed to the fourth decimal and a standardized procedure adhered to, the rate studies were reproducible to within 5 to 10%. This method seemed preferable to re-using the same catalyst specimen since the former procedure eliminated the possibility of accidental contamination. Both procedures were used however in the study of the fatty acids.

In actual practice 0.2000 g. of catalyst was placed in the hydrogenation vessel and then 25 ml. of absolute alcohol was added. The vessel was then flushed with hydrogen, closed and shaken for 15 minutes. During this time ap-

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[1] Presented before the Symposium on Catalysts held at the Diamond Jubilee Meeting of the American Chemical Society, September, 1951.

[2] O. Beeck, "Advances in Catalysis," Vol. 2, Academic Press, Inc., New York, N. Y., p. 151, 1950.

[3] L. Hernandez and F. F. Nord, *Experientia*, **3**, 489 (1947); *J. Colloid Sci.*, **3**, 363 (1949).

[4] A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2343 (1928).

[5] B. Zaar, Ber. Schimmel and Co., Akt. Ges. Jubilee Number, 299 (1929).

[6] L. Falaise and R. Frongnier, *Bull. soc. chim. Belg.*, **42**, 427 (1933).

[7] R. P. Linstead, *et al.*, *J. Chem. Soc.*, 740 (1931); 557 (1933).

[8] E. Schjanberg, *Ber.*, **70B**, 2385 (1937).

[9] E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 2156 (1929).