The Ozonation of Phenanthrene with Water as Participating Solvent

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Water acted as a participating solvent in the ozonation of phenanthrene in mixtures of aliphatic alcohols with water. The intermediate compound, a cyclic dihydroxy peroxide, was synthesized from diphenaldehyde and excess hydrogen peroxide. The extent to which water influenced the course of the ozonation reaction depended on the nature of the alcohol and the amount of water used with it. Diphenaldehyde was recovered directly from the aqueous solution of the ozonation products by removing the alcohol by atmospheric pressure distillation at pH below 7.5. The addition of chemical reducing agents was unnecessary. Diphenaldehyde showed surprising resistance to the action of mild oxidizing agents. When diphenaldehyde was oxidized with dilute nitric acid, phenanthraquinone was formed as principal product.

The primary objective of this work was the development of a procedure for the preparation of diphenic acid or diphenic acid precursors by treatment of phenanthrene with ozone under conditions which would pose no serious safety problems when adapted to large scale operation. It, therefore, seemed that the ozonation and the hydrolysis of the primary ozonation product must be made to take place concurrently in order to avoid accumulation of explosive ozonides or peroxides. Concurrent ozonation and hydrolysis meant that water must be present during the ozonation step, which in turn meant that classical low temperature ozonation techniques must be abandoned for higher temperatures at which water would be liquid regardless of the nature of the organic solvent and at which the hydrolytic reaction would be favored. Such conditions represented a radical departure from those which had been used in prior ozonations of arenes.[1]

When the conditions were examined in a preliminary way it was found that phenanthrene, suspended in a mixture of methyl alcohol and water, eagerly absorbed ozone at room temperature. It also was found that the product was not 2′-formylbiphenylcarboxylic acid (III) as recovered by Bailey[2] following the ozonation of phenanthrene in anhydrous methyl alcohol. After sodium hydroxide treatment of the ozonation product prepared in aqueous methanol, removal of the alcohol by distillation, and acidification of the distillation residue, the product was found to be a mixture of four compounds: III, 2′-hydroxymethyl-2-biphenylcarboxylic acid (VII), diphenide (the internal ester of VII shown as VIII), and diphenic acid. Further experiments showed that the relative yields of these compounds could be changed considerably by selection of particular aliphatic alcohols and the amount of water used with them as solvents for the reaction. Qualitatively, the effect of the presence of water during the ozonations was found to be the same with all of the aliphatic alcohols examined in that it favored the production of the biphenyl derivative in the lowest state of oxidation. Using the alkaline treatment described before, the biphenyl derivative favored was VII or VIII. Quantitatively, the effect of the presence of water during ozonation was different with different alcohols. Of those which were examined the effect on the nature of the product was greatest with *t*-butyl alcohol and least when methyl alcohol was used. A more important factor in determining the state of oxidation of the principal biphenyl derivative produced, however, was the pH of the aqueous solution during distillation to remove the alcohol. Regardless of the identity of the aliphatic alcohol and irrespective of the presence or absence of water during the ozonation step, the principal products were diphenaldehyde (V) and hydrogen peroxide when the pH was maintained below 7.5 during the distillation. In the diagrammatic representation of the series of reactions shown it seems to be certain that at least one intermediate compound was formed between phenanthrene and I or IV. From the standpoint of the Criegee mechanism of ozonation[1] the open chain compounds IX and X should have at least transitory existence. At one time it was believed that IX ($R = CH_3$) was the formula of the first isolable product of the ozonation of phenanthrene in anhydrous methyl alcohol,[2] but it was later shown[3-5] that the compound has the closed chain structure (I, $R = CH_3$). In the present work the dihydroxy peroxide (IV) was synthesized from diphenaldehyde and an excess of hydrogen peroxide. It was isolated, characterized, and then decomposed with sodium hydroxide to yield sodium 2′-hydroxymethyl-2-biphenylcarboxylate (VI), from which VII was obtained by acidification. Incidentally, we have found VII to be a material particularly suitable for use in the preparation of colorless diphenic acid. The intermediate IV has not yet been isolated directly from a product of the reaction of ozone with phenanthrene.

Diphenaldehyde was first prepared by Kenner and Turner[6] and almost coincidentally by F. Mayer.[7] Kenner and Turner showed that diphenaldehyde will undergo an internal Cannizzaro reaction on treatment with sodium hydroxide forming the sodium salt of the "alcohol acid" (VI). Mayer showed that diphenaldehyde will undergo a benzoin-type internal condensation when treated with potassium cyanide in boiling alcohol. Both reactions are typical of aromatic aldehydes. A completely anomalous behavior, then, was the resistance offered by diphenaldehyde to the action of mild oxidizing agents. Furthermore, we observed that, when diphenaldehyde was attacked by oxidizing agents, as for example by hot dilute nitric acid, the product was neither the "aldehyde acid" derivative (III) nor diphenic acid, either or both of which might be expected. Rather, the principal product was phenanthraquinone, presumably formed by the loss of an atom of hydrogen

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[1] P. S. Bailey, *Chem. Rev.*, **58**, 965 (1958).

[2] P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).

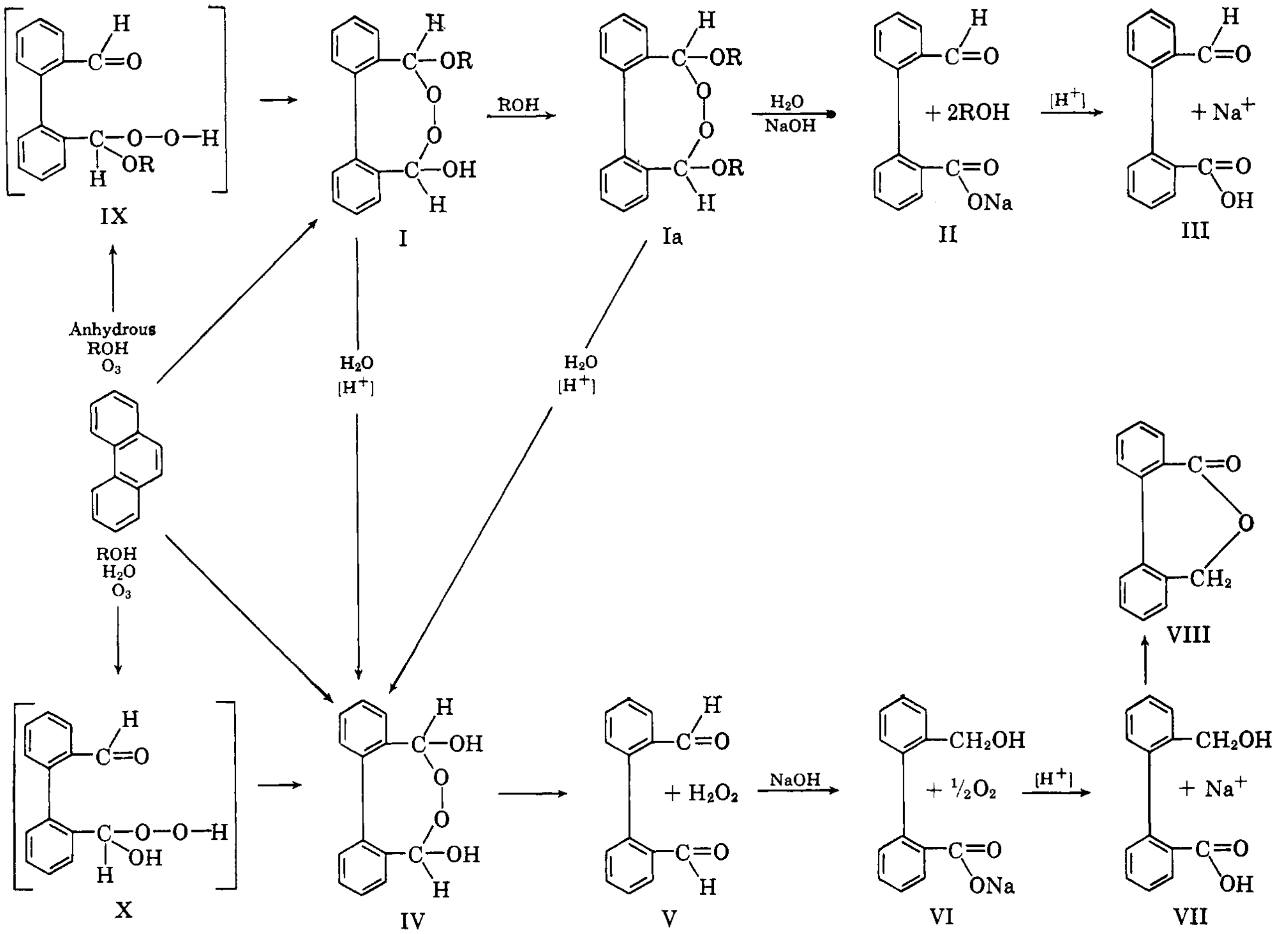
[3] J. P. Wibaut and T. J. deBoer, *Koninkl. Ned. Akad. Wetenschap. Proc., Ser. B.*, **59**, 421 (1956).

[4] P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **23**, 1089 (1958).

[5] J. P. Wibaut and T. J. deBoer, *Rec. trav. chim.*, **78**, 183 (1959).

[6] J. Kenner and E. Turner, *J. Chem. Soc.*, **99**, 2101 (1911).

[7] F. Mayer, *Ber.*, **44**, 2304 (1911); **45**, 1107 (1912).



from each of the aldehyde groups and ring closure. Previous authors[1–5] working with phenanthrene, methyl alcohol, and ozone took precautions to assure the anhydrous condition of the solvent. Decompositions of their ozonation products were carried out using sodium hydroxide. Under these conditions Bailey's methoxy peroxides were formed and the "aldehyde acid" (III) was the ultimate product. Diphenaldehyde was produced in quantity only when chemical reducing agents such as potassium iodide in acetic acid were added to the peroxidic reaction mixture.[8] Knowles and Thompson[9] suggested the use of trimethyl phosphite for this purpose.

Our work[10] has shown that the addition of reducing agents is not necessary. We find that, if water is added to the ozonation product of phenanthrene which has been formed at room temperature in anhydrous methyl alcohol and the alcohol subsequently recovered by distillation at pH below about 7.5, the principal products are diphenaldehyde and hydrogen peroxide. Diphenaldehyde is resistant to oxidation by hydrogen peroxide under the conditions of time, temperature, and concentration which obtain in the experiments. The active oxygen which persists in the absence of added reducing agents is accounted for by hydrogen peroxide. Table I illustrates the effect of the presence of water during the ozonation of phenanthrene in methyl alcohol, ethyl alcohol, and *t*-butyl alcohol. Methyl alcohol solutions containing more than 35% water are not satisfactory solvents for this reaction. When 50% aqueous methyl alcohol is used the solvent fails to wet the hydrocarbon crystals which are quickly floated to the surface of the column of liquid where they adhere to the walls of the tube and become unavailable for reaction. There is some attack on the solvent but most of the ozone passes through the absorption apparatus to the potassium iodide trap. Ethyl alcohol lies between methyl alcohol and *t*-butyl alcohol with respect to the composition of the mixture of biphenyl derivatives obtained in various alcohol and water mixtures. There can be little doubt that the explanation of these observations is that an equilibrium exists between the alkoxy peroxides of Bailey[2–5] and the dihydroxy peroxide herein described, the position of the equilibrium depending upon the nature of the alcohol and the amount of water present. In the event that the alcohol is removed by distillation prior to the addition of sodium hydroxide, the equilibrium is shifted far to the dihydroxy peroxide side. The dihydroxy peroxide decomposes to diphenaldehyde and hydrogen peroxide. Addition of reducing agents at this point simply destroys hydrogen peroxide. Addition of sodium hydroxide at this point converts the hydrogen peroxide to water and molecular oxygen and in addition brings about the Cannizzaro reaction V to VI. When sodium hydroxide is added to the ozonation product prior to the removal of the alcohol by distillation there is no broad shift in the equilibrium. The composition of the mixture of biphenyl derivatives observed as products is an indication of its position. Upon acidification of VI some VII may become dehydrated to diphenide (VIII). This dehydration is al-

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[8] P. S. Bailey and R. E. Erickson, *Org. Syn.*, **41**, 41 (1961).

[9] W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, **25**, 1031 (1960).

[10] M. G. Sturrock, E. L. Cline, and K. R. Robinson, U. S. Patent 2,942,030 (June 21, 1960).

TABLE I

OZONATION OF PHENANTHRENE IN ALIPHATIC ALCOHOLS AND THEIR MIXTURES WITH WATER

	Suspension medium		Composition of alkali soluble product estimated by infrared spectroscopy			
Experiment	Alcohol	% Water	% VII "Alcohol acid"	% VIII Diphenide	% III "Aldehyde acid"	% Diphenic acid
A	Methyl	0	0	0	100	0
B	Methyl	35	16	4	73	7
C	Ethyl	0	0	1	90	9
D	Ethyl	50	55	0	38	7
E	*t*-Butyl	0	0	0	98	2
F	*t*-Butyl	50	99	0	1	0

most quantitative when VII is boiled in an aliphatic alcohol. The manner of the origin of the diphenic acid which sometimes appears in the products has not been demonstrated conclusively.

Experimental

A Welsbach T-23 Ozonator was used to supply ozone to a reaction vessel of the column type described in the Welsbach Basic Manual. Because of the tendency of our hydrocarbon slurries to settle around and below the fritted area at the end of the gas inlet tube, the absorption apparatus was mounted on a magnetic stirrer. A Teflon-coated rod revolving at moderate speed served to lift the slurry to the level of the frit at which point the gas bubbles took over and kept the solids in adequately uniform suspension. The quantity of ozone absorbed in each experiment was determined in the manner described by Bailey.[2] In all experiments the rate of addition of the ozonized gas was adjusted to give substantially complete (90%+) absorption of the ozone. The phenanthrene was obtained from Gesellschaft fur Teerverwertung, Germany. It melted at 99-100° and was stated to be 99-100% pure. The alcohols were all reagent grade.

The following procedure was used to estimate the composition of the products. A 0.3-g. sample was weighed into a 10-ml. volumetric flask and diluted to mark with a 90:10 solution of carbon disulfide and dimethylformamide. The infrared spectrum was obtained using a Perkin-Elmer Model 21 double beam spectrophotometer. The proportions of III, VII, VIII, and diphenic acid were estimated by measurement of the 12.07-, 12.30-, 13.20-, and 13.53-μ absorbances and comparison with standard solutions of the pure compounds. The accuracy of this method was of course subject to the well known limitations of infrared spectroscopy imposed by the presence of four components. Except in those instances in which tarry materials were produced, it was sufficiently accurate for our purpose. Other identifications were made by melting points (corrected), carbon-hydrogen analyses, active oxygen (iodometrically), and estimation of hydroxyl group (acetyl chloride procedure) as indicated.

Mixture of *t*-Butyl Alcohol (88%) and Water (12%) as Solvent. Sodium Hydroxide Treatment of the Ozonation Product.—Fifteen grams (0.0840 mole) of phenanthrene was suspended in 109 g. of *t*-butyl alcohol and 15 g. of water was added. This is the azeotropic mixture. Ozonated air containing 1.512 g. of ozone per cubic foot was passed into the suspension at 25° at a rate of 0.02 ft.^{3}/min. Under these conditions 0.0843 mole of ozone was introduced of which 0.0840 mole was absorbed. Crystals of phenanthrene were no longer visible in suspension when about 75% of the total ozone had been introduced. The reaction product was transferred to a distillation apparatus and 100 ml. of 10% sodium hydroxide solution added carefully. The *t*-butyl alcohol was removed by distillation to vapor temperature 100°. Upon cooling, the aqueous distillation residue was extracted successively with three 25-ml. portions of benzene. Evaporation of the benzene gave 1.3 g. of material shown to be substantially phenanthrene. The aqueous solution was boiled to remove traces of benzene and the cooled solution acidified with dilute hydrochloric acid added dropwise. There was collected 16.4 g. of product, m.p. 120-123.5°. Examination of the material by infrared showed the presence of CH_2OH and COOH groups.

Anal. Calcd. for the alcohol acid (VII), $C_{14}H_{12}O_3$: C, 73.66; H, 5.39. Found: C, 73.32; H, 5.18.

Recrystallization of a portion of the crude product using acetone-hexane as solvent gave material, m.p. 141°, constant on recrystallization from the same solvent. Kenner and Turner[6] report m.p. 146° for VII. The infrared spectrum of the recrystallized products showed the presence CH_2OH and COOH groups. Recrystallization of a portion of the crude product using ethyl alcohol (95%) gave material, m.p. 134.5-135.5°. Examination of this product by infrared (solution and mull techniques) showed the presence of neither CH_2OH nor COOH groups. Kenner and Turner[6] reported m.p. 132° for diphenide (VIII).

Anal. Calcd. for VIII, $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.87; H, 4.80.

Yields of crude VII in this experiment were 85.4% based on the phenanthrene charged, 93.4% based on the phenanthrene reacted. Infrared examination indicated that the purity of the crude VII was about 75% and that the remainder was III and diphenic acid.

Mixture of *t*-Butyl Alcohol (50%) and Water (50%) as Solvent. Sodium Bicarbonate Treatment of the Ozonation Product.—Fifteen grams of phenanthrene was suspended in 63 g. of *t*-butyl alcohol and 63 g. of water was added. Ozone was introduced in the amount of 0.0945 mole of which 0.0883 mole was absorbed and 0.0062 mole recovered in the potassium iodide trap. Solid phenanthrene was present until about 90% of the ozone had been absorbed. The ozonation product was treated with 150 g. of 5% sodium carbonate solution and distilled to vapor temperature 98° in the manner previously described. From the weight and specific gravity of the distillate it was calculated that about 90% of the alcohol charged in the reaction tube had been recovered in the distillate. Upon cooling, the aqueous residue in the distillation flask deposited 14.4 g. of material, m.p. 58-62°, which was identified as impure diphenaldehyde (V). The yield was 81.4%. The material was identified by conversion to VII on boiling in dilute sodium hydroxide solution to which a small amount of ethyl alcohol was added to facilitate contact. The alcohol acid (VII) was identified by infrared examination and by conversion to VIII which was obtained in almost quantitative yield by boiling VII in 95% ethyl alcohol. The material in this experiment melted at 135-135.5°. The mixture melting point with a sample of VIII prepared in the preceding experiment was 134.5-135.5°. Further identification of V was by the preparation of the dioxime using the pyridine method.[11] Our product, crystallized from 95% ethyl alcohol, melted at 183-185°, constant on recrystallization. There is some disagreement in the literature about the melting point of this derivative. Mayer[7] and Criegee, *et al.*[12] reported 175-176°. Schmitt, *et al.*,[13] found 185-186°. Bailey[2] found 184-186°. Acidification of the sodium bicarbonate solution after removal of V gave 2.0 g. of high grade VII, m.p. 138-140°, unchanged on mixture melting point with an authentic sample of VII.

Anhydrous Methyl Alcohol as Solvent. Acid Work-Up Procedure Used on Ozonation Product.—The methyl alcohol was reagent grade absolute; no attempt was made to purify it. Five grams (0.028 mole) of phenanthrene was slurried with 100 g. of the alcohol. A stream of oxygen containing 4.12% ozone by weight was introduced at the rate of 0.01 ft.^{3}/min. until a total of 0.031 mole of ozone had been absorbed. The temperature of the mixture during reaction was between 0° and −20°. After ozonation 100 ml. of water was added and the alcohol removed as previously described. A yellow oil separated which solidified to a wax on cooling. The product was taken up in benzene. After evaporation of benzene 5.5 g. of solid, m.p. 59-62°, was obtained, equal to 93.3% of the theoretical weight of diphenaldehyde. A portion of the product was recrystallized from 70%

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(11) R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

(12) R. Criegee, B. Marchand, and H. Wannowins, *Ann.*, **550**, 99 (1942).

(13) W. J. Schmitt, E. J. Moriconi, and W. F. O'Connor, *J. Am. Chem. Soc.*, **77**, 5640 (1955).

aqueous ethyl alcohol. The recrystallized product melted at 62–63°. The identification of the product was confirmed by conversion to dioxime, m.p. 184–186°, and mixture melting point with a known sample of the derivative. The pH of the aqueous solution after benzene extraction was 3.5. It contained active oxygen which was determined iodometrically. The amount of active oxygen found was equal to 73% of that which would be expected from the hydrogen peroxide formed by the decomposition of 0.028 mole of IV.

Preparation of 4,5,6,7-Dibenzo-1,2-dioxa-3,8-cyclooctanediol (IV).—Three grams of pure diphenaldehyde (m.p. 63°) was stirred with 160 g. of 15% aqueous hydrogen peroxide for 1 hr. at 25°. At the end of this time substantially all the solid was in solution. The mixture was left overnight. The voluminous white precipitate which formed was separated by filtration, washed with a small amount of water and dried in a vacuum oven at 35°. The product melted at 105–106°. It was insoluble or only very slightly soluble in water at 25° and less than 2% soluble in 95% ethyl alcohol at that temperature. The yield was 3.1 g., (90%). In addition to the results of infrared examination which showed the presence of hydroxyl groups and the absence of carbonyl groups, the product had the following evidence of constitution.

Anal. Calcd. for IV, $C_{14}H_{12}O_4$: C, 68.8; H, 4.9; hydroxyl, 13.9; active oxygen, 6.6. Found: C, 68.3; H, 4.9; hydroxyl, 13.1; active oxygen, 6.3.

Erratic yields of IV were obtained with samples of V which were not too highly purified. It was found to be of advantage to heat the sample of V to 95° in a vacuum oven prior to mixing with the hydrogen peroxide. High yields (up to 95%) of IV were obtained consistently with material so treated.

Alkaline Decomposition of IV.—One gram of IV was refluxed with 100 g. of 5% sodium hydroxide solution for 2 hr. The clear solution was cooled to 5° and acidified to pH 1 by the dropwise addition of dilute hydrochloric acid. The slurry was held at 5° for 2 hr., then filtered, washed thoroughly with water, and dried in vacuum. The product weighed 0.90 g. and was identified as VII by its m.p. 143.5–144.5°. The melting point was unchanged when the product was mixed with an authentic sample of VII. The yield was 96%.

Oxidation of Diphenaldehyde with Dilute Nitric Acid.—One hundred grams of crude V, m.p. 58–62°, was refluxed with 1 l. of 35% (by wt.) nitric acid for 1 hr. The reaction mixture was cooled and the solids separated by filtration. The product was washed with water and then reslurried with warm 5% sodium hydroxide solution, separated again, washed thoroughly with water, and dried. Yield of phenanthraquinone, m.p. 203–205° (lit.[14] m.p. 206.5–207.5°), was 72.7%. Acidification of the alkaline solution gave 22 g. (19.1%) of crude diphenic acid, m.p. 214–220°, improved to 229–230° by recrystallization from 90% aqueous methanol. The literature[15] gives 229° as the melting point of diphenic acid.

Acknowledgment.—The assistance of Robert Mainier, Analytical Section, Research Department, Koppers Company, Inc., who performed the spectroscopic analyses, is acknowledged with gratitude.

(14) N. B. Lange, "Handbook of Chemistry," 10th Ed., McGraw Hill Book Co., Inc., 1961, p. 649.

(15) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," 5th Printing, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 172.

Rhenium Catalysts. VI. Rhenium(IV) Oxide Hydrate[1]

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Excess zinc in acid solutions in the presence of air reduces perrhenate to a finely divided black substance characterized as a hydrated rhenium(IV) oxide, probably $ReO_2 \cdot 2.5H_2O$. A survey of its catalytic activity in the hydrogenation of a variety of organic substrates is presented with particular attention to the selectivity of hydrogenation observed.

As a part of a research program directed toward a survey of the catalytic activity of rhenium compounds it has been found that zinc, tin, and iron, particularly zinc, readily reduce perrhenate in acid solutions in the presence of air to a very finely divided, insoluble, black hydrated rhenium(IV) oxide. The oxide was characterized by elemental analysis for rhenium and oxygen, dehydration, and oxidation state determination. The data obtained best support the formulation, $ReO_2 \cdot 2.5H_2O$, but do not preclude small variations from this composition.

The hydrate is very stable, indefinitely resisting dehydration at 95° over phosphorus(V) oxide *in vacuo*, and only very slowly losing water at 250°; however, when the hydrated oxide was heated with benzene at 250° under hydrogenation conditions, the recovered compound has the correct analysis for the anhydrous rhenium(IV) oxide, ReO_2. A small amount of water accompanied it as a co-product.

Young and Irvine[3] have reported the reduction of perrhenate with zinc and cadmium in hydrochloric acid solutions in the absence of air. They report the formation of $Re_2O \cdot 2H_2O$, using zinc as the reducing agent, and $ReO \cdot H_2O$, using cadmium, accompanied in either case by considerably larger amounts of rhenium(IV) not further characterized.

It has now been found that this hydrated rhenium(IV) oxide has activity as a hydrogenation catalyst. While this activity is much less than that of nickel or platinum catalysts in promoting the reduction of aromatic, olefin, carbonyl, and nitro groups, it is, on the other hand, much more effective than the platinum catalyst in promoting the reduction of the carboxylic acid function. This leads to a potentially valuable selectivity of reduction. Other rhenium oxides share this valuable property in varying degrees. Very few other elements show this characteristic in any degree.[4]

Table I summarizes the kind of results obtained in the hydrogenation of a variety of organic compounds using the hydrated rhenium(IV) oxide catalyst. Examples include compounds in which the olefin, carbonyl, nitro, and carboxyl moieties are represented, each alone, and in all but one of the possible binary combinations.

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(2) This paper is based on a portion of a thesis submitted by T. G. Selin (1957) in partial fulfillment of the requirements for the M.S. degree.

(3) R. C. Young and J. W. Irvine, Jr., *J. Am. Chem. Soc.*, **59**, 2648 (1937).

(4) *Cf.* papers III, VII, and VIII in this series: H. S. Broadbent, G. C. Shaw, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959); H. S. Broadbent and W. J. Bartley, *ibid.*, **28**, 2345 (1963); H. S. Broadbent and D. W. Seegmiller, *ibid.*, **28**, 2347 (1963).