also be of importance. One of these is the degree of swelling of the polymer droplets, which is variable throughout the course of conversion of monomer to polymer. It is reasonable to expect that the more highly swollen the droplets, the more probable is the fusion on collision. The data taken in this study offer no means for separation of effects of the latter types. For this reason, it is unprofitable to derive a more sophisticated relationship between particle size and the rate "constants" for particle combination.

A tendency toward greater stability of larger particles has been reported for butadiene-styrene latex systems in which the stabilizers are not adequate to prevent interparticle combination during polymerization.<sup>12</sup> In this study it was found that the larger particles under certain conditions would sweep up the smaller particles. However, where stabilization in similar systems is efficient, there is no evidence of a change in the number of particles with degree of monomer conversion.<sup>13</sup>

For vinyl acetate polymerization employing no stabilizer, the dielectric environment is seen to exert a large effect on the ultimate particle size and presumably on the combination during polymerization of the polymer droplets (Table IV). This is the expected result if it is assumed that the particles are stabilized by electrostatic charges, since these charges become effectively screened in the presence of electrolytes.

(12) C. E. Rhines and J. McGavack, Rubber Age, 63, 599 (1948).
(13) W. Smith, J. Am. Chem. Soc., 70, 3695 (1948).

The effect of electrolytes is much less marked (Table V) when a polyacid/salt stabilizer is employed in the production of vinyl acetate latices. In this mode of stabilization, the particles are doubtless kept from agglomerating by envelopes of polyacid/salt which present a hydrophilic surface to the suspending phase and inhibit fusion of the interior portions of the droplets, except under conditions of relatively high distortion from spherical shape.

While the mechanism of large-particle development by intercombination of polymer droplets has been examined only for polyvinyl acetate, it appears likely that the mechanism is quite general in all systems where the stabilizer available is not efficient or is not present in sufficient amount to cover the large area of interface present in latex systems of small particle size. In all of the examples examined in this study, the particle sizes are large compared to latices of the same materials prepared in the presence of surfactants, and in no case is there evidence of the existence of many very small particles.

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# THE CATALYTIC ACTIVITY OF REDUCED NICKEL MOLYBDATE AND REDUCED NICKEL CHROMATE<sup>1</sup>

# By J. ROOLEY, C. S. ROHRER AND O. W. BROWN

# Department of Chemistry, Indiana University, Bloomington, Indiana

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Reduced nickel molybdate and reduced nickel chromate were studied as catalysts for the vapor phase reduction of 1-nitropropane. The reduced nickel molybdate is a very good catalyst for this reduction, giving yields of propylamine as high as 94.8%. Using the reduced nickel chromate as a catalyst, propylamine is the primary product, giving yields up to 70.6%. Small amounts of propionamide are also produced, the yield increasing with an increase in the reaction temperature to approximately 8% at 240°. The activity of this catalyst is very sensitive to the time and temperature at which the nickel chromate salt is reduced.

Metals and their oxides have been classified in the order of their activities as catalysts in many reactions. Numerous additional investigations have been made as to the effect of various addition agents on the activity and structure of these catalysts.

One of the most intimate and homogeneous alterations to be affected in structure or interatomic distances should be made by the addition of a nonmetallic oxide to the metallic oxide catalyst such that a salt is formed. Yet there have been few studies on these compounds or the reduced metals obtained from these compounds as catalysts for the vapor phase reduction of organic nitro com-

(1) Contribution No. 556 from the Department of Chemistry at Indiana University.

pounds to their respective amines with hydrogen. It is hoped that the series will lead to a better understanding of the effect of these anions in modifying the activity of a catalyst and aid in predicting the behavior of an untried catalyst. Nickel molybdate and nickel chromate have been used as aromatization catalysts for hydrocarbons.<sup>2</sup> The chromate has been used to dehydrogenate and cyclize paraffin hydrocarbons<sup>3</sup> and to selectively hydrogenate butadiene to butylene in the gas phase.<sup>4</sup> The only catalyst reported for the reduc-

(2) Standard Oil Development Co., British Patent 594,569 (Nov. 13, 1947).

(3) A. Holter and A. C. Welty, U. S. Patent 2,392,738 (June 28, 1946).

(4) G. Natta, R. Rigamonti and P. Tone, Chem. and Industrie (Milan), 29, 235 (1947).

tion of nitropropane with hydrogen is reduced nickel tungstate.<sup>5</sup>

Apparatus.—A vertical type aluminum block furnace, electrically heated, thermally controlled and containing a 35-mm. Pyrex glass reaction tube was employed. Temperature was recorded by means of 2 thermocouples extending one inch into the catalyst bed from either end and a third extending well into the metal block. Feed was from above, controlled by the delivery of 2.00 ml. of 1-nitropropane under a variable head of mercury through a calibrated capillary tube. Hydrogen was measured in liters per hour through a calibrated flow meter.

Reduced Nickel Molybdate Catalyst.—The nickel molybdate catalyst was prepared by slowly adding a boiling solution, 90 g. of nickel nitrate hexahydrate in 500 ml. of water, to a boiling solution, 125 g. of sodium molybdate dihydrate in 500 ml. of water, to give a pale green nickel molybdate precipitate. An excess of the anion was used in an effort to prevent the formation of any nickel hydroxide whose presence would probably give a catalyst with abnormally high activity. X-ray diffraction studies gave no evidence of such in the precipitate. The freshly precipitated salt was washed until no trace of the nitrate ion was detectable and was then dried for 24 hours at 110°. Twenty grams of this salt was placed in the furnace, heated to a temperature of 405° and held there for one hour with 17 liters of hydrogen per hour flowing over the catalyst.

ing over the catalyst. X-Ray powder diffraction patterns show that the most prominent line appearing for the reduced catalyst corresponds to the *d*-value of the strongest line in the pattern for metallic nickel. The second and third strongest lines recorded for metallic nickel also appear in lesser intensities for the reduced catalyst giving a strong indication that this catalyst is to some extent metallic nickel. This confirms the findings of Woodman, Taylor and Turkevich<sup>6</sup> which through measurements of magnetic susceptibilities on this catalyst, prepared in a slightly different manner, indicated the presence of some dispersed nickel. The X-ray diffraction patterns gave no evidence for the presence of metallic molybdenum, and it is assumed that the anion is present in some partially reduced state.

The optimum temperature found for the reduction of the nitro compound is seen in Fig. 1 to be 145°. The operating conditions for the construction of this curve were 10 ml. per hour of nitropropane and a fivefold excess of hydrogen flowing over the catalyst.

#### TABLE I

Catalyst, 20 g. of nickel molybdate on 4 g. of asbestos reduced; furnace temperature, 145°

	Nitropropane, g. per hr.	Hydrogen in % excess	Amine in % converted
Α	6	500	86.2
	8	500	88.9
	9	500	93.2
	10	500	94.8
	11	500	93.0
	12	500	90.4
	14	500	87.8
в	10	300	89.8
	10	400	90.6
	10	500	94.8
	10	550	93.6
	10	600	92.9
	10	700	91.1

The rate of feed giving maximum yields was 10 ml. per hour of nitropropane, Table IA, and the optimum rate of flow of hydrogen was approximately 500% excess of nitropropane, Table IB.

This catalyst is seen to be an excellent one for the reduction of nitropropane to propylamine. It is of interest to note the 500% excess of hydrogen found for this reaction

(5) C. S. Rohrer, J. Rooley and O. W. Brown, THIS JOURNAL, 55, 211 (1951).

(6) J. F. Woodman, H. S. Taylor and J. Turkevich, J. Am. Chem. Soc., 62, 1397 (1940).



molybdate catalyst.

is the same value found when nickel tungstate was used as the catalyst.

Reduced Nickel Chromate Catalyst.—The eatalyst was prepared by slowly adding a boiling solution, 100 g. of nickel nitrate dihydrate in 500 ml. of water, to a boiling solution of 145 g. of sodium chromate decahydrate in 500 ml. of water. The precipitate formed was washed repeatedly until traces of the nitrate ion could be no longer detected. The moist salt was then dried in an oven for 24 hours at 110°. Twenty grams of the nickel chromate on 4 g. of shredded asbestos was placed in the furnace for reduction. Table II shows effects of the temperature, for reduction of this catalyst, on the yield of propylamine as recorded in the treatment of our original catalyst. A reduction temperature of 500° for a duration of approximately 10 hours was finally determined to give the catalyst of maximum activity.

#### TABLE II

Catalyst, nickel chromate; rate of hydrogen during reduction and heating, 17 liters per hour; rate of hydrogen during reduction of nitropropane, 250% of theory; rate of nitropropane, 10 ml. per hour; furnace temperature for the reduction of the nitropropane, 165°

Procedure in reducing the catalyst	Yield of 1st run in % converted	Average yield in % converted
Reduced at 415° for 1 hr.	56.7	54.0
Additional heating, 1.5 hours at 405°	79.0	57.9
Additional heating, 13 hours at 405°	85.5	66.8
Additional heating, 14 hours at 450°	87.6	62.7
Additional heating, 10 hours at 500°	90.1	70.6
Additional heating, 10 hours at 550°	72.8	55.1

Another point of interest is that in every case the yields of amine for the first run of nitropropane over the newly treated catalyst was appreciably higher than those obtained after several experiments where the yields became constant.

X-Ray powder diffraction measurements on the reduced nickel chromate show the three most prominent lines correspond to the *d*-values for the three most prominent lines of





metallic nickel. This again strongly indicates the catalyst contains considerable amounts of dispersed nickel. Since none of the *d*-values correspond to those reported for chromium, it is again assumed the anion is present in some partially reduced state. So far as can be determined by electron micrograph the size and shape of the particles are not changed by reduction, however they take on the appearance of being considerably more porous.

The primary products of the reduction of 1-nitropropane was n-propylamine with some propionamide. The optimum temperature for the production of the amine is seen from Fig. 2, curve A, to be from 165 to 175°, and the amide yield is seen to continually increase from 1.4% at 140° to 8% at 240° in Fig. 2, curve B. No attempt was made to increase the yield of the amide by further increase in temperature. The other variables show little or no effect on the yields of propionamide and all the experiments conducted at 165° gave approximately 2.6%. Feed of approximately 10 ml. of nitropropane per hour

Feed of approximately 10 ml. of nitropropane per hour gives the best yields, Table IIIA. The ratio of hydrogen to nitropropane giving the best yield is 250%, Table IIIB.

		IABLE III	
Catalyst,	, 20 g. nickel cl furnace	hromate on 4 g. temperature, 165	asbestos reduced;
	Nitropropane, g. per hr.	Hydrogen in % theory	Amine in % converted
Α	8	250	62.1
	9	250	66.8
	10	250	70.6
	12	250	61.6
в	10	200	67.5
	10	250	70.6
	10	300	67.1
	10	450	65.0
	10	500	64.7
	10	550	64.1

600

10

BLOOMINGTON, INDIANA

THE EXTENT OF THE PHOTOCHEMICAL REDUCTION OF PHOSPHOTUNGSTIC ACID

### BY LYMAN CHALKLEY

#### Received April 18, 1952

Phosphotungstic acid,  $H_3PW_{12}O_{49}$ , has been reduced by *i*-propyl alcohol under the influence of sunlight to a black product which precipitated silver from silver nitrate solution, while undergoing oxidation to the starting material. One molecule of  $H_4PW_{12}O_{49}$  after reduction precipitated one atom of silver from solution. Thus the reduced acid was in a state of oxidation equivalent to  $H_4PW_{12}O_{49}$ .

## Background

Like tungstic and molybdic acids,<sup>1</sup> silicotungstic and the 9 and 12 series phosphotungstic acids are photosensitive in presence of suitable reducing agents. Phosphomolybdic acid is also photosensitive. Rindl<sup>2</sup> reported the photosensitivity of "phosphotungstic acid" and concluded it to be due to a reaction of tungstic acid in dissociative equilibrium with the phosphotungstic acid. On the basis of preliminary experiments he postulated the formation of a blue tungsten oxide,  $W_5O_{14}$ . Rindl's identification of the oxide was tentative and based upon widely divergent analytical results.

# Discussion

It was observed that the color produced on photoreduction of the 12 series phosphotungstic acid, and also silicotungstic acid, was not the same as that produced by the reduction of tungstic acid. The product from tungstic acid is greener and of higher chroma ("brighter") than that from silicotungstic and the 12 series phosphotungstic acids. This observation threw doubt on Rindl's hypothesis as applied to the 12 series acids and led to a reexamination of the nature of the reduction product.

The reduced acid is reoxidized by air and by various other oxidizing agents. Thus there is a reciprocal relationship,  $H_3PW_{12}O_{40}$  + reducing agent + light  $\rightarrow$  reduced acid, and reduced acid + oxidizing agent  $\rightarrow H_3PW_{12}O_{40}$ , and the degree of reduction could be determined by measurement of the consumption of either the reducing agent or of the oxidizing agent required for the reverse process.

(1) Mellor, "Comprehensive Treatise on Inorganic Chemistry," 11, 537, 755 (1931).

Vasil'eva,<sup>3</sup> working with tungstic acid, and Rindl<sup>2</sup> with a phosphotungstic acid measured the quantity of oxidizing agent. The same approach has been followed in the present work but milder oxidizing agents have been used. For the problem is to oxidize the reduced tungsten compound without oxidizing the organic substances present.

In preliminary experiments gaseous oxygen was used as the agent. These experiments were made under conditions that did not permit of precise results and tended to give high readings of the oxygen consumed. Nevertheless they showed that the photochemical process stopped after two or three days exposure to sunlight. The highest oxygen consumption obtained was one atom of oxygen to 15 atoms of tungsten, indicating that  $W_4O_{14}$  was not the end-product of the reduction.

To attain greater precision, silver nitrate was used to oxidize the reduced phosphotungstic acid, and the precipitated silver was collected and determined. These determinations, like those made with  $O_2$ , indicated that the photochemical process terminated in a stable state after the action of sunlight for two to three days.

The results by this method were much more consistent than in the experiments with gaseous oxygen. Expressed in terms of atoms of tungsten in the form of reduced 12 series phosphotungstic acid required to reduce one silver ion, five determinations gave 10.9, 11.1, 11.8, 11.8 and 11.6 atoms of tungsten per atom of silver. The median was 11.6 and the average 11.4.

While not as precise as might be desired, these figures were sufficiently consistent to indicate a

(3) A. Vasil'eva, J. Russ. Phys. Chem. Soc., 44, 819 (1912); C. A., 6, 2886 (1912).

59.7

<sup>(2)</sup> M. Rindl, S. African J. Sci., 11, 362 (1916)