would be expected from the competition between the first-order reactions 5 and 8 and the second-order reactions 3 and 6 and provides further evidence that aldehydes arise from attack on an intermediate radical on a second alcohol molecule. On the other hand, the total yield of all three products drops. Since Fe^{3+} solutions in acetonitrile alone undergo photoreduction at almost the same rates as in the presence of alcohol, it appears that an additional primary photoreaction is occurring involving the acetonitrile, although this was not investigated.

In summary we conclude that the photooxidation of primary alcohols by Fe^{3+} involves excitation of a charge-transfer band and dissociation to alkoxy radicals, which in turn lead to the observed products by a sequence of well-established reactions. It thus parallels closely the photolysis at shorter wavelengths of aquoferric ion in water to yield hydroxyl radicals. What happens in concentrated aqueous systems, where the two paths might compete, has not been investigated, but, in view of the longer wavelength absorption of the alcohol complexes, products might well be wavelength dependent. In this regard, Carey, Cosgrove, and Oliver[11] have concluded that in the Fe^{3+} photooxidation of fairly concentrated solutions of ethylene glycol (0.5–2 M), their results are consistent with two reaction paths. One involves HO· attack on the glycol giving $HOCH_2\dot{C}HOH$ radicals which then undergo acid-catalyzed rearrangement and reduction to acetaldehyde,[12] and the other involves photolysis of a $Fe^{3+}\cdot$ glycol species to generate the alkoxy radical followed by β-scission to yield, eventually, two molecules of formaldehyde.

Experimental Section

Materials. Alcohols and reference compounds for analyses were commercial materials or prepared by standard synthetic methods. All were carefully purified and characterized by IR or NMR spectroscopy. Alcohols were dried by distillation from Na or $Mg-I_2$ under N_2. In spite of rigorous purification, some contained traces of aldehyde, and this was corrected for in the subsequent product analysis, using controls prepared from the same alcohol sample and put through the same workup cycle without irradiation. Iron was in the form of anhydrous $Fe(ClO_4)_3$ (G. Frederick Smith Chemical Co., ferric perchlorates, reagent, nonyellow). When copper was added it was in the form of $Cu(ClO_4)_2\cdot 6H_2O$.

Photolyses were carried out in Pyrex tubes immersed in a water bath at 16 or 21 °C, using a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well in the bath. Tubes were purged with argon for 30 min in the dark before irradiation. Reaction mixtures were in general 0.15 M in Fe and 0.015 M in Cu (when added). Photolyses were continued until solutions were colorless and tested for complete reduction of Fe^{3+} by testing an aliquot with aqueous ferrocyanide.

Workup and Analysis. When higher boiling components were to be analyzed, iron and copper were removed from reaction mixtures by passage through short alumina columns until the effluent gave negative tests with ferro- and ferricyanide. Low-boiling hydrocarbons were determined on separate samples in tubes sealed with serum caps. After photolyses these were chilled in dry ice, enough alumina was added to absorb metal ions, the tubes were recapped and warmed to room temperature, and samples for analysis were removed by means of a hypodermic syringe.

All analyses were by GC (gas chromatography), using internal standards with response factors calibrated against authentic reference compounds. Products from 1-pentanol, 2-methyl-1-butanol, and 2,2-dimethyl-1-butanol were identified by IR or NMR spectroscopy after isolation by preparative GC. Since all systems gave similar products, others were determined by retention time on one or more columns. Columns and internal standards that were found effective are summarized in Table III.

Yields are summarized in Tables I and II. Where experimental uncertainties are given, they represent the range of two or more independent experiments. In calculating yields, 2 mol of Fe was assumed to be consumed in the formation of RCHO and THF, and 1 mol in the formation of H_2CO, and total yield is taken as the sum of these. In cases where significant RCHO is formed via reactions 5 and 6, this gives a slightly high value.

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Registry No. 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 4-methyl-1-pentanol, 626-89-1; 4-phenyl-1-butanol, 3360-41-6; 2-methyl-1-butanol, 137-32-6; 2,2-dimethyl-1-butanol, 1185-33-7; Fe^{3+}, 20074-52-6.

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Comparison of the Activity and Lifetime of Raney Nickel and Nickel Boride in the Hydrogenation of Various Functional Groups

John A. Schreifels, P. Calvin Maybury,* and William E. Swartz, Jr.*

Department of Chemistry, University of South Florida, Tampa, Florida 33620

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Nickel borides (Ni_2B) are prepared by the reduction of a nickel salt with sodium borohydride. These materials have been shown to be active hydrogenation catalysts. The activity and lifetime of a P-1.50 nickel boride catalyst, which is prepared in a 50% water/ethanol solvent, are reported for the hydrogenation of unsaturated carbon and nitrogen bonds and for aldehydes. The data are compared to those obtained for similar reductions which employ Raney nickel as the catalyst. The nickel boride is more active and productive than Raney nickel in the hydrogenation of hexene, cyclohexene, and acrylonitrile. The properties of the two catalysts are similar for the reduction of cinnamaldehyde, 2-ethylhexanal, and benzaldehyde. The data for the reduction of nitrobenzene, adiponitrile, and propionitrile indicate that the nickel boride is more susceptible to nitrogen poisoning than Raney nickel.

The reduction of an inorganic nickel salt with sodium borohydride in solution gives a finely divided black precipitate that contains boron.[1] If the borohydride reduction is performed in aqueous solution, the product is referred to as a P-1.00 nickel boride. If the reduction is performed in 95% ethanol, the product is called P-2.00 nickel boride.[2,3]

Nickel borides have been shown to be very active catalysts in the hydrogenation of many functional groups. Russell et al.[4] have shown that P-2.00 nickel boride is very active in the hydrogenation of aldehydes. Marton and Alder have reported that the borides have high selectivity in the hydrogenation of ethylenic groups.[5] Russell and co-workers[6,7] have also studied the catalytic reduction of unsaturated compounds containing oxygen or nitrogen. The authors emphasize the utility of the boride catalyst on the basis of its ease of preparation, the lack of any catalyzed rearrangements and hydrogenolyses, slow carbonyl reductions, and lack of poisoning by amines. Further, Paul[8] studied the borides and compared their activity to that for Raney nickel in the solution phase hydrogenation of saffrole, furfural, and benzonitrile. The results of these studies indicate that the activity of the unpromoted nickel boride is equal to or slightly inferior to that of Raney nickel. Nickel boride has also been shown to be more resistant to degradation than Raney nickel. Brown and Brown[9] have demonstrated that the boride is considerably more active than Raney nickel toward hydrogenation of olefins. Recently, Strohmeier[10] has reported turnover numbers as high as 90000 for the nickel borides in the hydrogenation of some olefins, thereby demonstrating that boride catalysts are very durable.

An earlier report from our laboratory was concerned with the characterization of the surface of nickel boride catalysts via X-ray photoelectron spectroscopy (XPS).[11] The XPS data indicated that an oxidized form of boron as well as the expected boride were present on the catalyst surface. The relative amounts of these two forms of boron were a function of the method of preparation of the catalyst. For a P-2.00 nickel boride the oxidized boron dominates (oxide/boride ratio of $\simeq$10). For a P-1.00 boride prepared in aqueous solution, the boride is dominant on the surface (oxide/boride ratio of $\simeq$0.25). It was demonstrated that the oxidized form of boron could be removed via a water wash. This is consistent with the oxidized boron species being a borate salt. It is known that $NaBO_2$ may be produced as a side product in the reduction of a nickel salt with sodium borohydride to produce the nickel boride. Quantitative treatment of the XPS data allowed one to estimate that the $NaBO_2$ overlayer was approximately 36 Å thick for the P-2.00 nickel boride.

It was also found that when the nickel boride catalyst was employed for the reduction of acrylonitrile, the $NaBO_2$ overlayer catalyzed conversion of the substrate to 3-ethoxypropionitrile via a Michael-like addition while the boride catalyzed the hydrogenation to propionitrile.[11]

The $Ni(2P_{3/2})$ XPS spectra indicated that only one nickel species was present on the surface (Ni_2B). This species had a binding energy that was slightly smaller than that for elemental nickel. This suggests that the nickel in nickel boride is somewhat electron rich compared to Ni^0. The XPS data also indicated that the surface stoichiometry of the nickel boride was Ni_2B. This is consistent with the generally accepted bulk stoichiometry.

The present work is concerned with an evaluation of the activity and durability (lifetime) of the nickel borides in the hydrogenation of various functional groups. The nickel boride data will be compared with those obtained for similar hydrogenations with commercially available Raney nickel.

Experimental Section

Materials. All of the substrates were obtained from the Aldrich Chemical Co. The reagents were of the highest purity available (>98% purity). Prior to use, each compound was distilled and analyzed by gas-liquid chromatography to check the purity. Due to the very reactive nature of benzaldehyde and cinnamaldehyde, they were degassed with nitrogen prior to use. Nickel acetate, sodium borohydride, and kieselguhr were obtained from Ventron Corp. High-activity Raney nickel was obtained from Strem Chemical Co. The Raney nickel was in the form of a 50% slurry in water. The Strem specifications indicated that it contained 90% nickel, 9% aluminum, and traces of copper, iron, and magnesium.

Apparatus. The vessel used for preparation of the catalyst consisted of a 500-mL flask with a side arm. Attached to the side arm was a high-vacuum stopcock through which the sodium borohydride, wash solution, or solvent could be added without exposure to the atmosphere. The neck of the flask was fitted with a filtering adapter which consisted of a coarse-fritted funnel with a high-vacuum stopcock attached to the stem. A 24/40 ground-glass joint was attached to the mouth of the funnel. This apparatus allowed one to prepare the catalyst without atmospheric exposure.

The hydrogenations were carried out in a constant-pressure, Parr-like hydrogenator at a pressure of 6 atm and 70 °C. Since the reactions were run at an elevated pressure, it was assumed that no air would leak into the system and cause deactivation of the catalyst via oxidation.

Preparation of the Nickel Boride. A 0.8 M nickel solution was prepared by dissolving nickel acetate in the appropriate solvent (e.g., a P-1.50 catalyst would be made from a 50% ethanol-water solution). A 1.1 M solution of sodium borohydride was prepared in the identical solvent to which had been added 0.5 mL of 0.2 M sodium hydroxide solution. Once the sodium borohydride was completely dissolved, the resulting cloudy solution was filtered.

For the preparation of 1 mmol of catalyst, 12 mL of the nickel acetate solution was poured into the catalyst preparation flask. One milliliter of the filtered sodium borohydride solution was poured into the reservoir attached to the side arm of the flask. The reaction flask was attached to a vacuum line via standard-taper, ground-glass joints. Both the reservoir containing the sodium borohydride and the reaction flask were evacuated, and the reservoir was refilled with hydrogen.

Reduction of the nickel was accomplished by simultaneously shaking the reaction flask and opening the stopcock on the side arm. After the vigorous evolution of the hydrogen ceased, the reaction flask was isolated by closing the stopcocks on the fritted adapter and the side arm. The reaction flask was then disconnected from the vacuum system. Filtration was accomplished by connecting a vacuum line to the end of the fritted adapter, inverting the reaction flask, and opening the stopcock. After filtration was complete, the catalyst was washed twice with 5-mL aliquots of 95% ethanol. It should be noted that the catalysts had such a small average particle size that a significant amount of the catalyst would pass through the frit during filtration. Therefore, all of the catalysts were dispersed in kieselguhr to facilitate filtration. This was accomplished by mixing 1.00 g of kieselguhr with the nickel acetate solution for 10 min prior to reduction. XPS studies had previously shown that interactions between the nickel boride and kieselguhr were unlikely.

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Handling of the Catalyst. Standard glovebag techniques using dry nitrogen were employed to transfer the catalyst to the reaction flask to minimize any deactivation of the catalyst during transfer. For attachment of the reaction flask to the hydrogenator with a minimum of atmospheric exposure, the line connecting the reaction flask to the hydrogenator was evacuated while the sealing stopper was quickly replaced with the stopper attached to the hydrogen line. The flask was immediately evacuated.

The Raney nickel was obtained as an aqueous slurry. If the Raney nickel were vacuum dried and weighed in a drybox, considerable deactivation occurred. Therefore, the catalyst was dispensed as a slurry. After the reaction was complete, the Raney nickel was dried and weighed in order to determine the amount of catalyst employed in the reaction.

Since the Raney nickel was used as a slurry, it was necessary to remove the water prior to use. This was accomplished by washing the catalyst with absolute ethanol. This procedure did not adversely affect the catalytic activity. However, the activity of the catalyst was somewhat variable, depending on its age. In order to obtain results that were not biased by a significant change in activity with age, we always handled the catalyst in a nitrogen atmosphere and stored it under nitrogen in a freezer between reactions. The activity of the catalyst toward hydrogenation of 2 mol of acrylonitrile after it had aged for 4 months was compared with that of the same catalyst immediately after receipt. The activity of the aged catalyst was 1.36 while the activity of the fresh catalyst was 1.15. Thus, within experimental error (±15%), the activity of the catalyst had not changed over a 4-month period.

Surface Area Measurements. Surface area measurements were performed on a Quantachrome Monosorb surface-area analyzer. The catalyst was vacuum dried after being washed in the preparation flask. Once the catalyst was dry, the flask was brought to atmospheric pressure with hydrogen. The black powder was then transferred to a sample cell in a nitrogen-filled glovebag. The cell was sealed with the quick-inject adapter supplied with the instrument and transferred to the surface-area analyzer. After being degassed, the analyzer was calibrated by using dry nitrogen rather than air as recommended due to the pyrophoric nature of the nickel boride catalysts. Once calibrated, the surface areas were determined via standard BET procedures.

Product Analysis. The progress of the hydrogenations was measured by monitoring total pressure drop. Product analysis was performed via gas-liquid chromatography with a Varian Series 1400, temperature-programmable chromatograph equipped with a thermal-conductivity detector. The columns were 10% Carbowax 20M on Chromosorb W-HP and 10% OV-101 on Chromosorb W-HP. The products were identified by their retention times which were compared to those of known compounds for verification.

Results and Discussion

Catalytic Activity and Turnover Number. In the present study, the activity, $\bar{a}_t$, and turnover, UZ_t, numbers are those defined by Strohmeier.[10] The average activity is defined as the number of millimoles of product per millimole of catalyst per minute. The average activity during the first 60 min, $\bar{a}_{60}$, is defined as the catalyst's "average initial activity". A catalyst is assumed to be spent when, at less than 80% reaction, the average activity for the preceding 60 min is equal to 10% of the initial activity. The turnover number, UZ_t, is taken as the quantitative measure of the catalyst's lifetime. UZ_t is defined as the number of millimoles of product per millimole of catalyst at time t. Obviously, a very large turnover number is representative of a very durable catalyst. The substrate/catalyst ratio, K, is also of importance. If K is not significantly larger than UZ_t, there is a large possibility of error in the estimation of the ultimate turnover number.

The experimental error in activity and turnover number as determined from replicate measurements was ±15%.

Table I. Surface Areas and Catalytic Activities of the Nickel Borides[a]

catalyst	$\bar{a}_{60}$[b]	SA[c]	$\bar{a}_{60}$/SA
P-1.00	2.14	24.1	0.089
P-1.50	4.60	40.8	0.112
P-1.75	4.40	39.5	0.111
P-2.00	4.40	58.0	0.076
			0.097[d] (±18%)

[a] Conditions: substrate = acrylonitrile; pressure = 6 atm; temperature = 70 °C; $K = 1000$. [b] Units of activity = millimoles of substrate/(millimoles of catalyst × time (min)). [c] SA = surface area (m²/g). [d] Mean value.

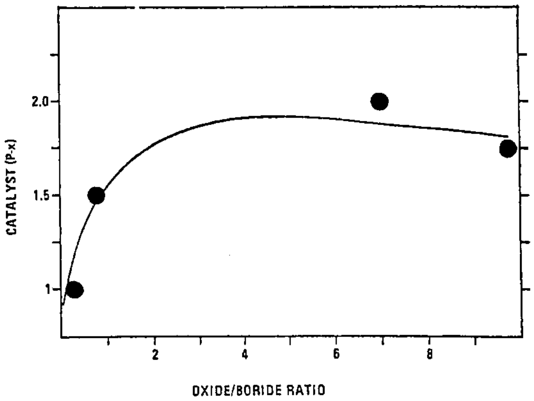

Figure 1. Variation of oxide/boride ratio as a function of catalyst preparation.

Effect of Surface Area on Catalytic Activity. Table I lists the catalytic activities of four nickel boride catalysts in the hydrogenation of acrylonitrile. It is well established that the activity of a catalyst can be correlated to its surface area. The surface areas obtained for the undispersed nickel borides are also listed in Table I. From the initial activities, $\bar{a}_{60}$, one must conclude that the activities of the P-1.50, P-1.75, and P-2.00 catalysts are essentially identical. The activity for the P-1.00 catalyst is significantly smaller. However, one must also note that the surface area for the P-1.00 catalyst is significantly smaller than those for the other catalysts. Normalization of the activity to surface area ($\bar{a}_{60}$/SA) gives an indication of the dependence of activity on surface area. The normalized activities show some variation but are relatively constant. It if is assumed that the normalized activities are constant, the mean is 0.097 with a relative standard deviation of 18%. The best precision obtainable on replicate surface area initial measurements was 5% while that for activity measurements was approximately 15%. Therefore, one must conclude that all of the undispersed nickel boride catalysts have the same normalized activity in the hydrogenation of acrylonitrile.

Choice of the Catalyst to be Studied. As discussed above, the activities of all of the nickel boride catalysts examined were essentially identical. However, it has been shown that the ethanol content of the solvent used to prepare the catalyst significantly affects the surface chemistry of boron in the nickel borides.[11] Figure 1 is a plot of oxide/boride ratio as a function of catalyst preparation. Note that the P-1.75 and P-2.00 catalysts contain a thick overlayer of oxidized boron which has been identified as $NaBO_2$. This borate overlayer has been shown to interfere in the hydrogenation of acrylonitrile.[11] The P-1.50 catalyst has a much thinner borate overlayer. In addition, if surface areas are considered as discussed above, the P-1.50 catalyst is 100% more active than P-100. Therefore, the P-1.50 catalyst was chosen for the comparison with Raney nickel.

Establishing a Reference Point for Comparisons. If one is to compare catalytic activities using a P-1.50

Table II. Activities and Lifetimes of Raney Nickel and P-1.50 Nickel Boride/Kieselguhr in the Hydrogenation of Carbon-Carbon Multiple Bonds

run	substrate	catalyst	K	$\bar{a}_{60}$	$\bar{a}_t$	UZ_t	% reaction	t, min
1	acrylonitrile	P-2.00^{a,b}	4000	4.30	2.75	496	12.4	180
2			1000	4.10	1.94	350	35.0	180
3		P-1.50^{b}	1000	4.60	2.13	970	97.0	455
4			12500	2.60	0.95	1191	9.5	1253
5		R-Ni^{b}	1175	1.20	0.27	380	32.0	1407
6			1800	1.10	0.36	526	29.0	1460
7	1-hexene	R-Ni	285	0.89	1.04	226	79.0	217
8			425	0.26	1.10	370	87.0	334
9			1000	1.25	0.46	145	14.5	315
10			1438	8.62	3.46	971	67.0	280
11		P-1.50	500	3.0	1.33	411	82.0	309
12			1818	14.5	7.70	1773	97.0	230
13			10000	35.9	17.50	6656	67.0	380
14			10732	51.2	26.50	5174	48.0	154
15	cyclohexene	R-Ni	429	0.40	0.08	129	30.0	1502
16			333	0.52	0.08	128	37.0	1471
17		P-1.50	500	0.54	0.24	334	67.0	1393
18			500	0.54	0.28	362	72.0	1292
19	cinnamaldehyde	R-Ni	141	0.13	0.02	62	44.0	2800
20			81	0.20	0.04	65	80.0	1440
21		P-1.50	141	0.41	0.07	58	41.0	383
22			500	0.47	0.13	80	16.0	610
23	2-butyne-1,4-diol^{c}	R-Ni	130	0.088	0.074	121	93.0	1653
24			71^{d}	0.028	0.017	60	85.0	3640
25		P-1.50	143^{d}	0.152	0.054	137	96.0	1275

[a] Strohmeier et al.[10] [b] P-2.00 = P-2.00 nickel boride in kieselguhr; P-1.50 = P-1.50 nickel boride in kieselguhr; R-Ni = Raney nickel. [c] Dissolved in ethanol (total volume 250 mL). [d] Hydrogenated at room temperature.

catalyst with previously reported data, a common point of reference must be established. Strohmeier's study[10] of the activity of a P-2.00 nickel boride catalyst in the hydrogenation of acrylonitrile can be used for reference. Strohmeier's data and the present data for P-1.50 nickel boride will be evaluated relative to those for the identical reaction with Raney nickel. These data are also included in Table II.

For a substrate/catalyst ratio (K) of 100. Strohmeier obtained an activity ($\bar{a}_{60}$) of 4.0 and a lifetime (UZ_t) of 350. When these data are compared with those of the P-1.50 catalyst, the initial activity (4.6) of the P-1.50 is only slightly greater. However, the lifetime (970) is nearly three times as large as that of Strohmeier's P-2.00 catalyst. These data indicate that the procedures employed in the production of P-1.50 nickel boride in this laboratory are at least as effective as those used elsewhere.

Also listed in Table II are data from the hydrogenation of acrylonitrile with Raney nickel. Notice that for similar values of K (e.g., 1175 for Raney nickel and 1000 for nickel boride) the initial activity for Raney nickel is nearly one-fourth that of the boride. Furthermore, the final activity for Raney nickel is nearly one-tenth that of the nickel boride. The turnover number for Raney nickel (380) is approximately one-third that of the P-1.5 (970). Thus, the P-1.50 nickel boride catalyst offers approximately a threefold advantage in terms of activity and productivity over Raney nickel in the hydrogenation of acrylonitrile.

Hydrogenation of Other Olefins. Table II also contains data for the hydrogenation of other olefins. Difficulties were encountered in obtaining consistent results with 1-hexene. The initial activity for run 7 was 0.89, while the final activity was 1.04. The Raney nickel was initially not very active. The activity then increased and finally decreased to zero. This behavior is not well understood. However, more reasonable results were obtained by allowing the Raney nickel to soak in ethanol during the wash stage as demonstrated in runs 9 and 10 where the final activities were at least 50% of the initial activity. If water was not removed from the pores of the catalyst during the washing step, then, considering the relative densities of 1-hexene and water, the water would be replaced very slowly with 1-hexene and hydrogen. If one compares run 10 with run 12, it can be seen that the initial activity and turnover number of Raney nickel are smaller than those of nickel boride. In this case, Raney nickel has only reached 67% reaction. This suggests that the ultimate turnover attainable for Raney nickel in the hydrogenation of 1-hexene is approximately 1000. The nickel boride catalyst, however, did not stop at 67% reaction until it had a turnover number of approximately 6000 (runs 13 and 14).

The initial activity of nickel boride in the hydrogenation of cyclohexene was very similar to that for Raney nickel. However, the P-1.50 catalyst had a larger turnover number. The average turnover number of 348 is approximately 3 times greater than that for Raney nickel (128). Comparison of the hydrogenation of 1-hexene to that of cyclohexene by using a P-1.50 catalyst indicates that the initial activities differ by a factor of 6. Wade et al.[12] have reported activities which differed by at least a factor of 40 for a P-3.00 catalyst (which was prepared by a totally different method). Thus, it appears that the selectivity is strongly dependent on the method of preparation.

Nickel boride is initially threefold more active than Raney nickel in the hydrogenation of cinnamaldehyde. In terms of overall durability, however, there is little difference between the two catalysts. In the hydrogenation of cinnamaldehyde there is the possibility of obtaining a number of different reaction products. Russel et al.[7] have concluded that borohydride-reduced nickel and palladium exhibit an almost ideal selectivity for only one of several potentially reducible groups in a molecule. In their studies, with $K = 5$, only hydrocinnamaldehyde was obtained. In the present study with $K = 141$, a small amount of cinnamyl alcohol (~5%) was obtained. This suggests that the selectivity of a nickel boride catalyst has a small dependence on the substrate/catalyst ratio. Rylander[13] has

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Table III. Catalytic Activities and Lifetimes of Raney Nickel and P-1.50 Nickel Boride/Kieselguhr in the Hydrogenation of Aldehydes

run	substrate	catalyst	solvent[a]	K	$\overline{a}_{60}$	$\overline{a}_t$	UZ_t	% reaction	t, min
1	2-ethylhexanal	R-Ni[b]	ethanol	95	0.26	0.19	81	85	422
2				222	0.19	0.10	200	90	1970
3		P-1.50[b]	ethanol	133	0.36	0.13	127	95	960
4				185	0.28	0.13	131	70	990
5	benzaldehyde	R-Ni	none	112	0.076	0.024	101	90	4245
6				159	0.033	0.008	11	1	1313
7		P-1.50	none	250	0.234	0.069	83	33	1210
8				500	0.234	0.108	39	8	360
9	dextrose	R-Ni	ethanol/water[c]	6.9	0.0080	0.0025	3.7	53	1440
10		P-1.50	ethanol/water[c]	6.9	0.0380	0.0062	6.9	100	1040

[a] Volume of solvent + volume of aldehyde = 250 mL. [b] R-Ni = Raney nickel. P-1.50 = P-1.50 nickel boride in kieselguhr. [c] 80% ethanol/20% water.

discussed similar observations for other catalysts. It is also worthy of note that at $K = 141$ for Raney nickel, approximately the same amount of cinnamyl alcohol was produced.

As previously reported,[14] saturation of an acetylenic bond occurs in stepwise fashion (eq 1). With few exceptions, the intermediate olefin is largely of cis configuration.

$$\text{alkyne} \xrightarrow{H_2} \text{olefin} \xrightarrow{H_2} \text{parafin} \qquad (1)$$

In the hydrogenation of 2-butyne-1,4-diol (runs 23–25) the cis configuration was dominant (~99%) when a sample of the reaction mixture was analyzed via gas chromatography at a point slightly beyond the reaction of 1 equiv of hydrogen. After the reaction of 1 equiv of hydrogen, the hydrogenation rate increased fivefold. These observations were noted for both Raney nickel and nickel boride. The later observation has previously been attributed to a very strong adsorption of the acetylene group on the catalytic sites.[15] The acetylenic functional group will then occupy the available sites, causing preferential hydrogenation of the acetylenic group even though other readily reduced groups are present.[16]

The initial activities in the present case are consistent with the suggestion that the P-1.50 nickel boride catalyst is more active than Raney nickel in the hydrogenation of 2-butyne-1,4-diol. A comparison of the lifetimes of the catalysts was impossible since the activities were so low. However, the data indicate that both Raney nickel and P-1.50 nickel boride are able to attain turnover numbers of at least 120 in the hydrogenation of 2-butyne-1,4-diol.

Hydrogenation of Aldehydes. The activities and lifetimes of P-1.50 nickel boride and Raney nickel catalysts in the hydrogenation of various aldehydes are listed in Table III. In each case, the initial activity of the nickel boride was greater that for Raney nickel. In addition, the activities of the two catalysts were more nearly equivalent for those aldehydes which were easily reduced. One must also note that the turnover numbers of both catalysts are significantly smaller when an aldehyde is reduced than when an olefin is reduced.

The data suggest that Raney nickel has a longer lifetime than nickel boride in the reduction of 2-ethylhexanal. One must also note the effect of K on the lifetime. As the amount of substrate per unit of catalyst increased, the turnover number increased likewise (compare run 2 with run 1).

The reproducibility of the lifetime data for the reduction of benzaldehyde with Raney nickel (runs 5 and 6) and nickel boride is poor, even though the initial activities are relatively constant. It is likely that this may be attributed to the strong adsorption of benzaldehyde onto the catalytic surface with a subsequent loss of active sites.

The reduction of dextrose to sorbitol presented some problems. Since both catalysts had low activities, a true lifetime could not be measured. In addition, the solubility of dextrose dictated the use of a mixed solvent. It must be noted, however, that the nickel boride had an initial activity that was approximately 5 times as large as that for Raney nickel. It must also be pointed out that the hydrogenation with Raney nickel stopped at 53% reaction while that with nickel boride went to completion.

Hydrogenation of Compounds with Nitrogen Multiple Bonds. Since compounds containing unshielded nitrogen atoms are known to act as inhibitors, the catalytic hydrogenation of nitrogen-containing compounds is of particular interest. The inhibiting effect of the nitrogen atom is limited to those instances where it exists as a base capable of donating electrons. For example, in the case of NO_2 or CN groups, the nitrogen should have little or no effect on the catalytic activity. However, reduction of each of these functional groups to the amine produces compounds which should effect catalytic activity. Thus, the relative resistance of a catalyst to nitrogen poisoning can be determined by studying the reaction kinetics during the course of the hydrogenation.

The RNO_2 functional group is one of the easiest groups to reduce.[17] Therefore, it should be possible to attain relatively high turnover numbers in the reduction of nitro compounds. The results for the hydrogenation of nitrobenzene with Raney nickel and nickel boride are listed in Table IV. For $K = 137$, the turnover number with Raney nickel was 96 (70% reaction). On the other hand, nickel boride only underwent 12% reaction with a turnover number of 16. One must note, however, that the initial activities of the two catalysts were approximately equal. Russell et al.[6,7] have shown that boride catalysts resist amine poisoning. However, the reduction of nitro groups in neutral or basic media may also result in the formation of azo, hydrozo, and/or azoxy compounds. It is possible that the production of such side products is responsible for the observed poisoning of the catalysts. The poisoning

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(13) P. N. Rylander, "Catalytic Hydrogenations over Platinum Metals", Academic Press, New York, 1967, p 52.

(14) Reference 13, p 59.

(15) R. L. Augustine, "Catalytic Hydrogenations", Marcel Dekker, New York, 1965, p 71.

(16) G. F. Hennion and S. O. Barnett, *J. Am. Chem. Soc.*, **79**, 2146 (1957).

(17) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, 1972, p 9.

Table IV. Catalytic Activities and Lifetimes of Raney Nickel and P-1.50 Nickel Boride/Kieselguhr in the Hydrogenation of Nitrogen Multiple Bonds

run	substrate	catalyst	solvent	K	$\overline{a}_{60}$	$\overline{a}_t$	UZ_t	% reaction	t, min
1	nitrobenzene	R-Ni[a]	none	137	0.230	0.049	96	70	1940
2				166	0.168	0.032	158	95	4870
3		P-1.50[a]	none	500	1.30	0.12	106	22	857
4				137	0.24	0.13	16	12	120
5	adiponitrile	R-Ni	ethanol	13.3	0.0098	0.0024	1.2	9	513
6			ethanol/NH_4OH[b]	7.5	0.034	0.0162	6.6	90	422
7			ethanol/NH_4OH[b]	19.6	0.043	side reaction occurred			805
8		P-1.50	ethanol	13.3	0.053	0.035	11.6	87	330
9			ethanol/NH_4OH[b]	19.6	0.047	0.014	18.7	96	1330
10			ethanol	19.6	0.061	0.042	17.2	88	413
11			ethanol/water[c]	19.6	0.062	0.052	15.3	78	292
12	propionitrile	R-Ni	ethanol/NH_4OH[b]	12	0.123	0.096	12	100	125
13			ethanol/NH_4OH[b]	61	0.106	0.100	61	100	605
14			ethanol	46	0.103	0.108	46	100	430
15			ethanol/NH_4OH[b]	12	0.066	0.108	11	95	175
16			ethanol/NH_4OH[b]	61	0.079	0.028	26	43	923
17			ethanol	46	0.211	0.097	46	99	475
18			ethanol/water[c]	46	0.300	0.120	40	86	333

[a] R-Ni = Raney nickel; P-1.50 = P-1.50 nickel boride in kieselguhr. [b] Millimoles of NH_4OH/millimoles of substrate = 5.0. [c] 60% ethanol/40% water.

is more extensive for the nickel boride than for Raney nickel.

The reduction of the nitrile functional group is complicated by the possibility of side reactions. A mechanism has been proposed for the formation of secondary and tertiary amines in which the hydrogenation proceeds through an imine intermediate[18] (eq 2). The addition of

$$\underset{\text{nitrile}}{RCN} \xrightarrow{H_2} \underset{\text{imine}}{RCH{=}NH} \xrightarrow{H_2} \underset{\text{amine}}{RCH_2NH_2} \qquad (2)$$

the primary amine to the intermediate imine gives a product from which the secondary amine can be formed by hydrogenolysis. Tertiary amines (eq 3 and 4) may be

$$RCH{=}NH + RCH_2NH_2 \rightleftarrows RCH(NH_2)NHCH_2R \qquad (3)$$

$$RCH(NH_2)NHCH_2R + H_2 \rightarrow (RCH_2)_2NH + NH_3 \qquad (4)$$

formed primarily through the addition of a secondary amine to an imine followed by hydrogeolysis. With low molecular weight nitriles, secondary and tertiary amines may be greatly favored while larger nitriles may give fair yields of the primary amine.[19] Secondary and tertiary amines may be prevented, or least minimized, by performing the reduction in the presence of at least 5–6 molar equiv of ammonia in acidic medium or in the presence of an acylating agent.[20] Ammonium hydroxide can be used, but the presence of a large amount of water causes some hydrolysis of the imine formed in the reduction process, leading to secondary amine formation.

The hydrogenation of dinitriles leads to the formation of diamines unless five- or six-membered-ring formation is possible through an intramolecular amine–imine condensation. Use of Raney nickel to catalyze the reduction of succinonitrile has been reported to give a high yield of pyrrolidine.[21] In addition, hydrogenation to one amine can occur. For example, the hydrogenation of equal weights of adiponitrile, ammonia, and toluene over palladium on silica at 4500 psig and 110 °C gave a 92% yield of 5-cyanopentylamine[22] (eq 5).

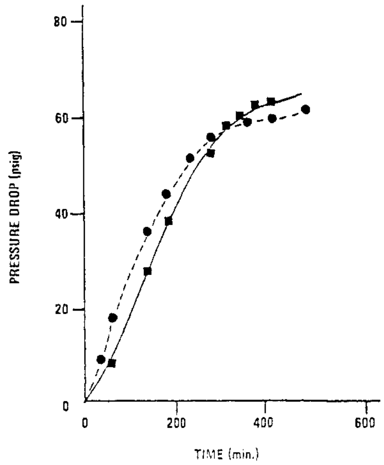

Figure 2. Pressure drop as a function of time for the reduction of propionitrile over nickel boride (●) and Raney nickel (■) catalysts.

$$NC(CH_2)_4CN + 2H_2 \rightarrow H_2N(CH_2)_5CN \qquad (5)$$

In light of these data, reductions of adiponitrile were performed. The data (Table IV) indicate that the initial activity of nickel boride was higher than that of Raney nickel by about 50% and that 100% of the substrate reacted in each case. However, a side reaction occurred in each case. The percentage of reaction for runs 6–11 was calculated on the basis of the amount of the desired product formed. A different side reaction occurred to a very large extent (>50%) in run 7. The unexpected product eluted from the column after the diamine and before the dinitrile. The side product present in all of the other reactions eluted after water and well before the diamine. None of the side products were isolated or identified.

It should be noted that the reaction employing nickel boride as the catalyst with ammonium hydroxide and ethanol as the solvent (run 9) gave the greatest overall yield of the desired product with only 4% side reaction. Under

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(19) A. Giner-Sorolla and A. Bendich, *J. Am. Chem. Soc.*, **80**, 3932 (1958).

(20) M. Freifelder, "Catalytic Hydrogenations in Organic Synthesis", Wiley Interscience, New York, 1979, p 43.

(21) H. P. Schultz, *J. Am. Chem. Soc.*, **70**, 2666 (1948).

(22) P. N. Rylander, "Catalytic Hydrogenations over Platinum Metals", Academic Press, New York, 1967, p 218.

Table V. Product Distribution in the Hydrogenation of Propionitrile with Raney Nickel and P-1.50 Nickel Boride/Kieselguhr

run	catalyst	K	solvent	yield, %			
				PA[a]	DPA[a]	TPA[a]	PN[a]
12	R-Ni[c]	12	ethanol/NH$_4$OH[b]	100	0	0	0
13	R-Ni	62	ethanol/NH$_4$OH[b]	100	0	0	0
14	R-Ni	46	ethanol	70	30	0	0
15	P-1.50[c]	12	ethanol/NH$_4$OH[b]	95	0	0	5
16	P-1.50	62	ethanol/NH$_4$OH[b]	43	0	0	57
17	P-1.50	46	ethanol	78	21	0	1
18	P-1.50	46	ethanol/water[d]	86	0	0	14

[a] PA = propylamine; DPA = dipropylamine; TPA = tripropylamine; PN = propionitrile. [b] Millimoles of NH$_4$OH/millimols of substrate = 5.0. [c] R-Ni = Raney nickel; P-1.50 = P-1.50 nickel boride in kieselguhr. [d] 60% ethanol/40% water.

identical conditions, the Raney nickel hydrogenation was complicated by the formation of the extra side product discussed above (run 7).

As is evidenced by a higher initial activity, the reduction of propionitrile with both catalysts was easier than that for adiponitrile. The initial activity of nickel boride was approximately half that of Raney nickel when ammonium hydroxide was added (runs 12 and 13 vs. 15 and 16). On the other hand, when no ammonium hydroxide was added, nickel boride was more than twice as active as Raney nickel. This again suggests that nickel boride was poisoned to a larger extent than Raney nickel by the amine product.

Figure 2 is a plot of the kinetic data (pressure drop vs. time) for runs 14 and 17. As amine concentration increases with time, the rate of reduction with the nickel boride catalyst decreases to a larger extent than that with Raney nickel. At approximately 90% reaction, the Raney nickel becomes more active than the nickel boride. As stated above, there is a distinct possibility that secondary or tertiary amines are being formed. The product distribution observed in the hydrogen of propionitrile is listed in Table V. Initially, no propionitrile was detected for any of the hydrogenations employing Raney nickel. However, all of the hydrogenations employing nickel boride as the catalyst contained propionitrile. The data suggest that under identical conditions Raney nickel will more completely hydrogenate the nitrile than will the boride.

Secondary, but no tertiary, amines were produced only in those hydrogenations which employed absolute ethanol as the solvent. Nickel boride produced slightly less secondary amine than Raney nickel. These results can be compared with those of Barnett[23] in which a significant amount of secondary amine was obtained under similar conditions. This may partially be attributed to a difference in reaction rate. Barnett's reaction time for $K = 15$ was 26 h. Reactions 12 and 15 were completed in approximately 2 and 3 h, respectively.

Conclusions

(1) The surface area of a nickel boride catalyst is a definite contributing factor to its catalytic activity in hydrogenation reactions. (2) Nickel boride is more active and productive than Raney nickel in the hydrogenation of carbon–carbon multiple bonds. (3) The activity and productivity of nickel boride in the reduction of aldehydes is similar to that for Raney nickel. (4) The substrate/catalyst ratio (K) can be very important in determining the productivity of a catalyst. (5) Nickel boride catalysts are more susceptible to poisoning by unshielded nitrogen compounds than Raney nickel. (6) In the hydrogenation of compounds with nitrogen multiple bonds, a P-1.50 nickel boride catalyst can be made to produce only the primary amine by selection of the proper solvent.

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Registry No. Raney nickel, 7440-02-0; nickel boride, 12007-01-1; nickel acetate, 373-02-4; sodium borohydride, 16940-66-2; acrylonitrile, 107-13-1; 1-hexene, 592-41-6; cyclohexene, 110-83-8; cinnamaldehyde, 104-55-2; 2-butyne-1,4-diol, 110-65-6; 2-ethylhexanal, 123-05-7; benzaldehyde, 100-52-7; dextrose, 50-99-7; nitrobenzene, 98-95-3; adiponitrile, 111-69-3; propionitrile, 107-12-0; propylamine, 107-10-8; dipropylamine, 142-84-7.

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(23) C. Barnett, *Ind. Eng. Chem., Prod. Res. Dev.*, 8, 145 (1969).