

This very simple preparation of an active nickel catalyst, together with its low isomerizing tendency, promise to make this catalyst a very useful one for laboratory hydrogenations.

This study was assisted in part by a Research Award (585C) from the Petroleum Research Fund of the American Chemical Society.

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RECEIVED JANUARY 11, 1963

THE REACTION OF SODIUM BOROHYDRIDE WITH NICKEL ACETATE IN ETHANOL SOLUTION—A HIGHLY SELECTIVE NICKEL HYDROGENATION CATALYST

Sir:

We wish to report that the reaction of sodium borohydride with nickel acetate in ethanol solution produces a colloidal black material, presumably nickel boride,^{1,2} which exhibits remarkable selectivity in the hydrogenation of olefins of different structural types. Moreover, it exhibits an unusually low tendency to isomerize olefins during the hydrogenation. Consequently, this catalyst promises to be exceedingly useful for the selective hydrogenation of one olefin in the presence of another, for the selective hydrogenation of the more reactive double bond of a diene and for the conversion of internal acetylenes into *cis* olefins of high purity.³

TABLE I
RATES OF HYDROGENATION^a OF REPRESENTATIVE OLEFINS OVER NICKEL BORIDE (P-2)

Olefin	Time (min.) for hydrogenation ^b	
	10%	50%
1-Octene	1	7
1-Pentene	1	9
3-Methyl-1-butene	2	15
3,3-Dimethyl-1-butene	8	56
2-Methyl-1-butene	35	(400)
<i>cis</i> -2-Pentene	10	120
<i>trans</i> -2-Pentene	40	(360)
Cyclopentene	2	10
Cyclohexene	30	(200)
Cyclooctene	4	28
Styrene	2	9
Safrole	1	3.5

^a Hydrogenation of 40 mmoles of olefin at 25°, 1 atm. pressure, in ethanol, over catalyst prepared from 5.0 mmoles of nickel acetate. ^b Values in parentheses are estimated by extrapolating the experimental data.

The experimental procedure is exceedingly simple. The nickel acetate, 5.0 mmoles, was dissolved in approximately 40 ml. of 95% ethanol contained in the usual hydrogenation flask. The flask was connected to the hydrogenation apparatus⁴ and flushed with 1 l. of hydrogen by introducing the required quantity of sodium borohydride solution into the generator flask. The catalyst was produced by injecting 5.0 ml. of a 1.0 M solution of sodium borohydride in ethanol to the rapidly stirred solution of nickel acetate. Hydrogenation was then initiated by introducing 40 mmoles of the olefin with a hypodermic syringe.

It was observed that safrole underwent hydrogenation with a half-life of 3.5 min., approximately twice the

(1) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

(2) R. Paul, P. Buisson and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).

(3) The designation P-2 is proposed to differentiate this selective nickel boride catalyst from the highly active catalyst (P-1) prepared in aqueous solution: C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 1003 (1963).

(4) C. A. Brown and H. C. Brown, *ibid.*, **84**, 2829 (1962). This apparatus is now available from the Delmar Scientific Laboratories, Inc., 317 Madison Street, Maywood, Illinois.

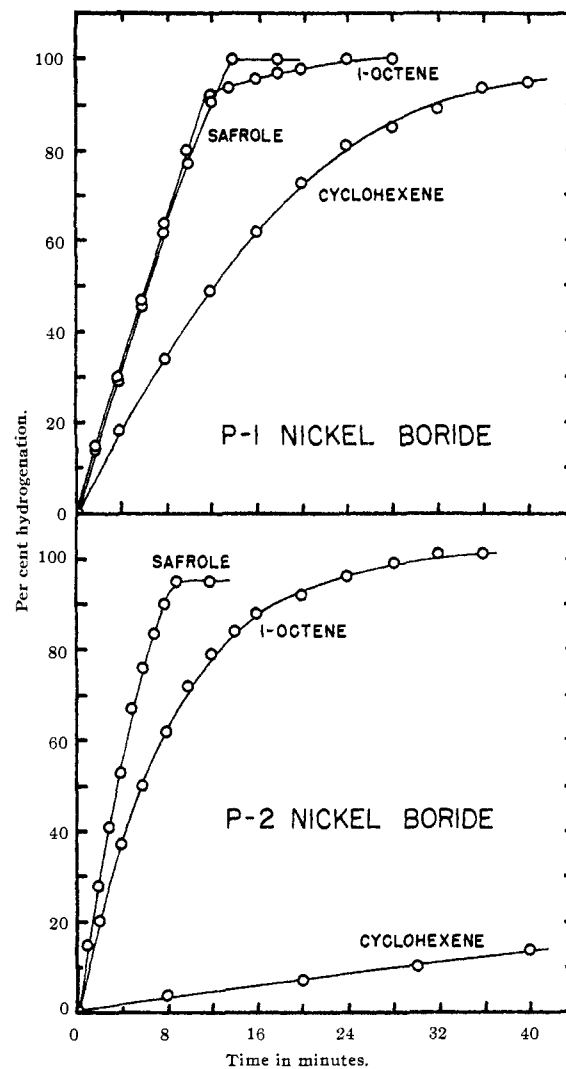


Fig. 1.—Rates of hydrogenation at one atmosphere pressure and 25° of 40 mmoles of safrole, 1-octene and cyclohexene over 5.0 mmoles of P-1 and P-2 nickel boride.

rate observed with the P-1 catalyst. The half-life for 1-octene was 7 min., very similar to that realized with the P-1 catalyst. Finally, the rate with cyclohexene was exceedingly slow, with a half-life of approximately 200 min., in contrast to the 12-min. half-life observed with the P-1 catalyst (Fig. 1). Consequently, this catalyst, prepared in ethanol, achieves a major spread in rates, as compared to that observed with platinum,⁵ Raney nickel³ or the P-1 nickel boride.³

A detailed study revealed that the catalyst is indeed highly sensitive to the structure of the olefin (Table I).

Moreover, this catalyst is remarkably free from isomerization tendencies (Table II).

TABLE II
ISOMERIZATION OF 1-PENTENE IN THE COURSE OF HYDROGENATION^a AT 25° IN ETHANOL OVER P-2 NICKEL BORIDE

Hydrogenation, %	Product, mmoles			
	1-Pentene	<i>cis</i> -2-Pentene	<i>trans</i> -2-Pentene	<i>n</i> -Pentane
0	40	0	0	0
26	28.9	0.6	0.1	10.4
52	18.5	.7	.1	20.7
79	7.2	.9	.2	31.7
100	0	0	0	40

^a Hydrogenation of 40 mmoles of olefin at 1 atm. pressure over catalyst prepared from 5.0 mmoles of nickel acetate.

(5) H. C. Brown and C. A. Brown, *ibid.*, **84**, 2827 (1962).

To test the ability of the catalyst to hydrogenate selectively, a mixture of 40 mmoles each of 1-pentene and 2-methyl-1-butene was hydrogenated to the absorption of 40 mmoles of hydrogen. The product contained 49% *n*-pentane, 1% 1-pentene, 1% 2-methylbutane and 49% 2-methyl-1-butene. Similarly, the half hydrogenation of 2-methyl-1,5-hexadiene and 4-vinylcyclohexene produced better than 95% yields of 2-methyl-1-hexene and 4-ethylcyclohexene.

The hydrogenation of 3-hexyne proceeded rapidly to the absorption of 50% of the hydrogen required to saturate the compound, and very slowly beyond. Gas chromatographic examination of the product at the 50% point revealed the formation of *cis*-3-hexene in a purity of 98–99%.

These results indicate that this catalyst should be very useful for selective hydrogenations in synthetic chemistry.

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TETRAHEDRAL NiCl_4^{2-} IN MOLTEN SALTS. THE COMPLETE SPIN-ALLOWED SPECTRUM OF 3d ORBITAL TRANSITIONS

Sir:

We have measured the complete spin-allowed spectrum of 3d orbital transitions for NiCl_4^{2-} in solution in molten salts at high temperatures. These measurements include the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition near 4000 cm^{-1} , which, though rarely observed, is an important diagnostic test for tetrahedral Ni^{2+} complexes. The NiCl_4^{2-} spectrum was observed for solutions of NiCl_2 in CsCl and KCl melts. The results are typified by the spectrum shown in Fig. 1, which is for a solution in CsCl at 680°.

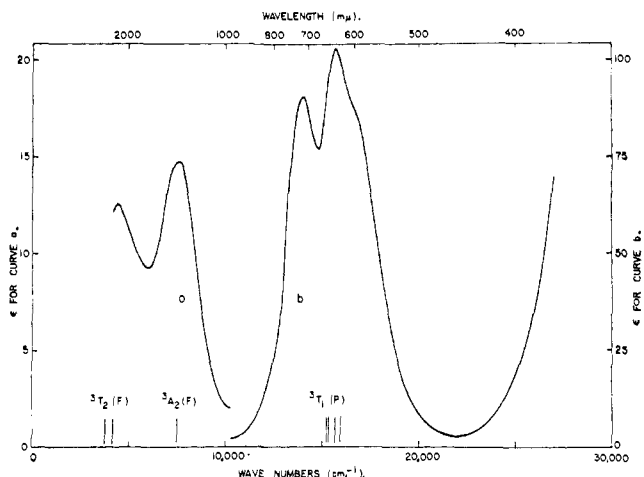


Fig. 1.—Absorption spectrum of NiCl_2 dissolved in molten CsCl at 680°. The molar extinction coefficient scale for the visible spectrum, curve b, is on the right while the scale for the infrared spectrum, curve a, is on the left. Computed values of the excited-state energy levels for $Dq = 370 \text{ cm}^{-1}$ are indicated immediately above the wave-number scale.

Three spin-allowed orbital transitions are predicted for tetrahedral Ni^{2+} complexes, ${}^3T_1(F) \rightarrow {}^3T_2(F)$, ${}^3A_2(F)$, ${}^3T_1(P)$. Measurement of all three transitions is required to check ligand-field theory. Liehr and Ballhausen¹ calculated the energies of these transitions, including spin-orbit fine structure, as functions of Dq .

(1) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)*, **6**, 134 (1959).

The spectrum in Fig. 1 fits the Liehr and Ballhausen calculations for a Dq of about 370 cm^{-1} and also agrees with that measured by Weakliem² for Ni^{2+} impurity ions at tetrahedral sites in a Cs_2ZnCl_4 crystal. The bands in the melt are decidedly broader than those in the crystal, presumably because of the high temperatures.

The importance of measurements of the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition for the identification of tetrahedral nickel(II) complexes in molten salts is the following. The spectra of tetrahedral and octahedral complexes of d^2 -configuration ions are similar since three regions of spin-allowed absorption in the visible and near-infrared are predicted for both structures. Two spectral characteristics have been proposed as tests to distinguish between them. First, the ligand-field splitting of the 3F term is only about half as great for a tetrahedral complex as for the corresponding octahedral complex, which means that an absorption band should occur in the 4000–5000- cm^{-1} region for tetrahedral fields but not for octahedral fields. Second, the intensity of the tetrahedral spectrum should be much greater than that of the octahedral spectrum because of the absence of an inversion center in a tetrahedral field. The utility of this latter test for nickel(II) complexes in molten salts is a cloudy issue at present. Until recently it was supposed that the intensity of an electronically allowed transition is at least 10^2 times that of a vibronic transition.³ However, the electronically allowed transitions of tetrahedral (or approximately tetrahedral) NiCl_4^{2-} in organic solvents^{4,5} prove to be no more than 30 times as intense as the vibronic transitions of, for example, the octahedral hexaquo nickel(II) ion.⁶ Furthermore, all of the nickel(II) complexes in molten salts that have been reported to be octahedral^{7,8} have anomalously intense spectra so that the bands reported here for tetrahedral NiCl_4^{2-} are only about twice as intense.⁹

Previous measurements of the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition have been confined to nickel-doped inorganic crystals^{2,10} and the $\text{NiI}_2(\text{P-}n\text{-Pr-Ph}_2)_2$ complex dissolved in CH_2Cl_2 .¹¹ The NiCl_4^{2-} complex has been studied in non-fused-salt solutions^{4,5,12} and in crystals with organic cations¹³ but the reported spectra do not include the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transition.

Gruen and McBeth⁷ proposed that the tetrahedral NiCl_4^{2-} complex is formed when NiCl_2 is dissolved in fused CsCl, Cs_2ZnCl_4 and pyridine hydrochloride. This proposal was based on measurements of the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ band in the visible region. The present measurements leave little room for doubt that this proposal is essentially correct, although Furlani and Morpurgo⁵ point out that the complex structure of the visible band may indicate that the NiCl_4^{2-} ion is mildly distorted from the configuration of a regular tetrahedron.

(2) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(3) See, for example, T. M. Dunn, "The Visible and Ultra-Violet Spectra of Complex Compounds," in "Modern Coordination Chemistry," edited by J. Lewis and R. G. Wilkins, Interscience Publishers, New York, N. Y., 1960, p. 379.

(4) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(5) C. Furlani and G. Morpurgo, *Z. Physik. Chem. (Frankfurt)*, **28**, 93 (1961).

(6) C. Furlani, *ibid.*, **10**, 291 (1957).

(7) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

(8) K. E. Johnson and T. S. Piper, *Discussions Faraday Soc.*, **32**, 32 (1961).

(9) For a discussion of the anomalous intensity of octahedral complexes in melts, see D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

(10) R. Pappalardo, D. L. Wood and R. C. Linares, Jr., *J. Chem. Phys.*, **35**, 1460 (1961).

(11) R. G. Hayter, Mellon Institute, private communication.

(12) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960).

(13) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).