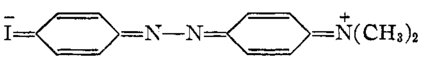
or slightly lower than, the value predicted. The large decrement (−0.38) observed in the *p*-OCH_3 compound may be the result of the contribution of structures of type IV which would in effect raise the -OCH_3 group moment above that derived from substituted anisoles; in agreement with this the moment of *p*-methoxyazobenzene (1.48) is larger than that of anisole (1.23).

Both *p*-chloro and *p*-iodo-*p*′-dimethylaminoazobenzene show a slight enhancement of resonance, increments of +0.21 and +0.39, respectively, being observed. Since a decrease might be anticipated due to the contribution, in the azobenzene series, of structures of type IV not possible in the halobenzenes, the observed increments may be significant. It is possible that by expanding their octets the halogens can act as electron-receiving groups; in the presence of a good electron-donating group resonance forms of type V may then be important enough to give rise to the observed increments.[16] A similar increment has been observed with the *p*-halogen substituted dimethylanilines[17] and is, as above, largest with the iodo compound


V

as would be expected since iodine has the greatest tendency to expand its octet.

[16] "Iodine-bond resonance" was suggested first by Pauling to account for interatomic distances in *p*-diiodobenzene; see H. P. Klug, *J. Chem. Phys.*, **3**, 747 (1935).

[17] R. J. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

EAST LANSING, MICHIGAN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Catalytic Activity of Metals Produced by the Reduction of Salts in Liquid Ammonia. II. Nickel[1]

BY GEORGE W. WATT, WILBUR F. ROPER[2] AND SIDNEY G. PARKER[2]

Studies on the preparation and properties of nickel hydrogenation catalysts formed by the reduction of nickel(II) bromide with potassium in liquid ammonia show that the ammonia-insoluble reduction products include (in addition to elemental nickel and nickel amide) a potassium-containing substance that reacts with ethanol (the hydrogenation reaction medium) and with allyl alcohol (one of the hydrogen acceptors employed) and influences both the rate and mechanism of the hydrogenation of the latter.

It was reported earlier[3] that nickel from the reduction of nickel(II) bromide with potassium in liquid ammonia exhibits appreciable activity as a catalyst for the hydrogenation of allyl alcohol. More detailed studies are described in the present paper. Catalysts prepared in liquid ammonia, W-6 Raney nickel, and nickel from the reduction of nickel(II) oxide with hydrogen are compared in terms of surface areas, adsorbed hydrogen and hydrogenation rate measurements.

Experimental

Materials.—Nickel(II) bromide 6-ammonate was prepared as described by Watt.[4] Allyl alcohol was generously supplied by the Shell Chemical Corporation. Physical constants found (literature[5] values in parentheses): b.p. 96.7–96.9° cor. (96.90–96.98°); $n^{25}D$ 1.4108 (1.4111). Hexene-1 (research grade, purity 99.22 ± 0.10%) obtained from the Phillips Petroleum Co. was used without further purification.

Preparation of Nickel Catalysts.—W-6 Raney nickel was prepared as described by Adkins and Billica,[6,7] stored under absolute ethanol at 0°, and at all times protected from the atmosphere.

Nickel was prepared from nickel(II) oxide by reduction with predried hydrogen[8] at known temperatures within the range 265–310°, cooled to room temperature in an atmosphere of dry hydrogen, and thereafter protected from exposure to the atmosphere. The nickel content of these products ranged from 96.0 to 97.5%.

The preparation of nickel catalysts by the reduction of nickel(II) bromide (used in the form of the 6-ammonate) with solutions of potassium in liquid ammonia was carried out using equipment and procedures described elsewhere.[9,10] Variables in addition to those investigated previously[3] were studied in an effort to produce catalysts having a nickel content comparable to those from the reduction of nickel(II) oxide with hydrogen. From runs employing from 1.5 to 3.0 g. of nickel(II) bromide 6-ammonate dissolved and suspended in from 12 to 65 ml. of liquid ammonia, and reduction with 2 to 4 gram atoms of potassium/mole of bromide, ammonia-insoluble products having a wide range of composition were obtained, *i.e.*, Ni, 47–90%; N, 2–13% and K, 10–28%. In 10 runs for which complete analytical data are available, analyses for these three elements account for an average of 94% of the gross ammonia-insoluble product. In addition to the range of variables indicated above, frequency of agitation and repetition of addition of potassium were also studied. In the latter experiments, the initial solid reduction products were washed with liquid ammonia, resuspended in ammonia and treated with excess potassium in an unsuccessful effort to reduce the by-product nickel(II) amide to elemental nickel.[11] The product of highest nickel content (90%) was obtained by reducing 2.0 g. of the bromide in 12 ml. of ammonia with 0.75 g. of potassium; the solid product was washed seventeen times with 20-ml. portions of ammonia. All transfers of solid catalyst samples were made in an inert oxygen-free atmosphere in a dry-box.

Surface Area Measurements.—Surface areas were measured by a modification[12] of the method of Brunauer, Emmett and Teller. Values found for nickel prepared in liquid ammonia ranged from 5 m.²/g. for a product containing 67% Ni to 8 m.²/g. for one containing 84% Ni. Simi-

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[1] This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

[2] Field Research Laboratories, Magnolia Petroleum Co., Dallas, Texas.

[3] G. W. Watt and D. D. Davies, THIS JOURNAL, **70**, 3753 (1948).

[4] G. W. Watt, *Inorganic Syntheses*, **3**, 194 (1950).

[5] Shell Chemical Corporation, "Allyl Alcohol," Tech. Publication 46-22, Knight-Counihan Co., San Francisco, p. 42, 1946.

[6] H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 695 (1948).

[7] Data on the composition of W-6 Raney nickel catalysts will be published elsewhere.

[8] V. Ipatieff, *J. prakt. Chem.*, **77**, 513 (1908).

[9] G. W. Watt and T. E. Moore, THIS JOURNAL, **70**, 1197 (1948).

[10] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

[11] W. M. Burgess and J. W. Eastes, *ibid.*, **63**, 2674 (1941).

[12] H. E. Ries, R. A. Van Nordstrand and W. E. Kreger, *ibid.*, **69**, 35 (1947).

larly, the area of nickel from nickel(II) oxide was found to be 17 m.²/g., while that of W-6 Raney nickel was 87 m.²/g.

Measurement of Adsorbed Hydrogen.—Hydrogen adsorbed on or otherwise associated with the nickel catalysts was measured as follows. Samples contained in an especially designed Pyrex glass sample tube attached to a Toepler pump were heated to known temperatures as high as 550°, or until gas evolution ceased. The gas was pumped off and collected over mercury in a gas buret attached to a gas analysis train. Reduction products of nickel(II) bromide having widely different compositions yielded from traces up to 29 cc. H_2/g., 26–83 cc. NH_3/g. and 2–34 cc. N_2/g. Under identical conditions nickel from nickel(II) oxide yielded no hydrogen over periods up to 8 hr. W-6 Raney nickel that had aged 2 to 12 months gave 40 to 74 cc. H_2/g.; the average was 59 cc./g.

Catalytic Activity.—The activity of the three different types of nickel catalysts was evaluated in terms of the rate of hydrogenation of allyl alcohol using a modification of the apparatus described by Joshel.[13] Practically all rate data were obtained using 14.63 millimoles of allyl alcohol (0.850 g.) in 10.0 ml. of absolute ethanol at 30.0 ± 0.5°, at a hydrogen pressure of 1500 ± 5 mm., and with agitation at a frequency of 930 r.p.m. To eliminate induction periods, catalysts prepared in ammonia were pretreated with hydrogen for 15 min. prior to introduction of the acceptor; nickel from nickel(II) oxide[14] was similarly pretreated for 30 min.

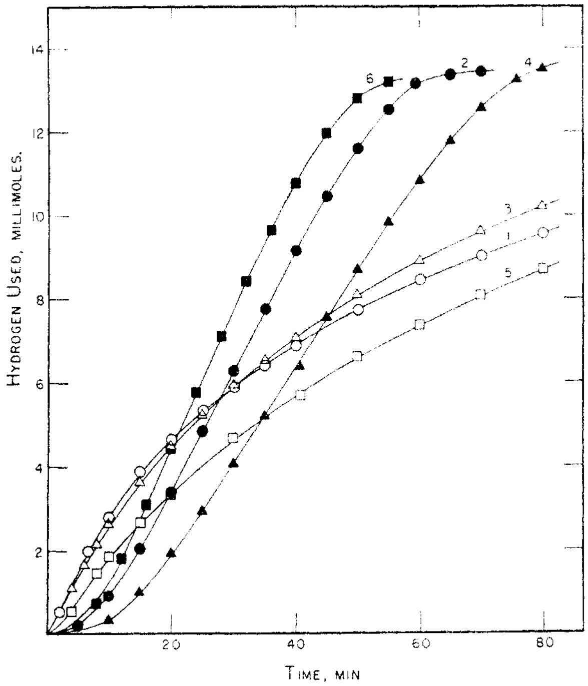

Fig. 1.—Hydrogenation of allyl alcohol over Ni from $NiBr_2$: ○, raw catalyst; ●, washed; △, KOC_2H_5 added; ▲, washed; □, KOH added; ■, washed, 40°.

Data which show that the catalytic activity of nickel from nickel(II) bromide is essentially independent of the composition of the ammonia-insoluble reduction product are given in Table I. These data show also the extent of purification accomplished by washing with ethanol; attempts to identify the impurities thereby removed, by means of X-ray diffraction patterns, were unsuccessful.

The rate of hydrogenation of allyl alcohol over nickel prepared in liquid ammonia is shown for a typical case by curve 1 in Fig. 1. In this run, 0.120 g. of a catalyst containing 66.6% Ni, 6.3% N, and 22.9% K was used. Upon completion of the hydrogenation, the nickel was held at the bottom of the flask with the stirrer magnet and the solution and suspension of impurities was drawn off under conditions that obviated exposure to the atmosphere. The catalyst was then washed 8 times with 10-ml. portions of absolute ethanol and subsequently used for the run shown as curve 2. In an effort to reproduce the rate behavior characteristic of the raw catalyst, the nickel was again washed as described above and used for another hydrogenation after addition of potassium ethoxide at a concentration equivalent to the potassium content of the raw catalyst (curve 3, Fig. 1). The potassium ethoxide was then washed out with ethanol and the washed catalyst was used in the run represented by curve 4. The above sequence was repeated using potassium hydroxide in place of potassium ethoxide (curve 5). Finally, the potassium hydroxide was removed by washing with ethanol and the washed catalyst was used for a hydrogenation at 40° (curve 6). The catalyst finally recovered weighed 0.060 g. and contained 98.0% Ni; the loss in weight includes both impurities and elemental nickel unavoidably lost during the many washing operations.

TABLE I

COMPOSITION AND ACTIVITY OF CATALYSTS PREPARED IN LIQUID AMMONIA

Catalyst [a]wt., mg.	Nickel content, % [b]Raw catalyst	[c]After use	[d]($\Delta m/\Delta t$)
81	71.3	..	0.14
94	57.0[e]	..	.14
96	79.6	..	.14
88	75.0	95.5	.17
90	86.6	96.0	.18
67	90.5	96.2	.16
60	66.6[e]	98.0	.11

[a] Weight determined after use in hydrogenation runs. In most cases the weights of raw catalysts were known and the decrease in weight occasioned by washing with ethanol (see footnote *e*) paralleled closely the composition of the raw catalyst. Thus, about 60 mg. was lost in washing the raw catalyst that contained 66.6% Ni, while only 14 mg. was removed from that containing 90.5% Ni. [b] *I.e.*, the ammonia-insoluble reduction product sampled without exposure to the atmosphere or to absolute ethanol. [c] Catalyst washed with *ca.* 80 ml. of absolute ethanol. [d] Values in terms of millimoles of hydrogen consumed/min., after reaction had proceeded for 30 min. [e] In cases involving reduction products of low elemental nickel content, there was visual evidence of reaction upon contact with absolute ethanol.

The above results indicate that the raw catalyst contains an impurity which solvolyzes upon contact with ethanol to form potassium ethoxide. Such an impurity could similarly give rise to the potassium salt of allyl alcohol, thereby altering diffusion rate, adsorption characteristics, or other rate-controlling steps involving the hydrogen acceptor. Accordingly, hydrogenation runs using 1.346 g. (0.016 mole) of hexene-1, an acceptor not susceptible to the complications suggested above, were made under conditions already specified. The data shown in Fig. 2 support the assumptions made with reference to the nature of the impurity in the raw catalysts.

A comparison of the rates of hydrogenation of allyl alcohol over W-6 Raney nickel, nickel from nickel(II) oxide, and nickel from the reduction of nickel(II) bromide with potassium in liquid ammonia is shown in Fig. 3.

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(13) L. M. Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943). Although designed for analytical purposes, this equipment has been found adaptable to the procurement of reliable rate data. In preliminary studies with W-6 Raney nickel, the maintenance of steady state conditions over at least 75% of the total reaction time was demonstrated repeatedly. Variables investigated included temperature, hydrogen pressure, agitation frequency, ratio of catalyst to acceptor and acceptor to solvent, concentration of the hydrogenation product, and age of the catalyst. That these studies led to substantially the same conclusions reached by others [see, for example, (a) J. Bougault, E. Cattelain and P. Chabrier, *Bull. soc. chim.*, [5] **5**, 1699 (1938); (b) H. A. Smith, W. C. Bedoit and J. F. Fuzek, THIS JOURNAL, **68**, 229 (1946)] who used other types of equipment serves further to establish the reliability of the methods employed in the present work.

(14) These products were found to be totally inactive as catalysts for the hydrogenation of allyl alcohol when the oxide was reduced at 300–310°. Catalysts reproducible with respect to both composition and activity result when the oxide is reduced at 265–285°; *cf.* Ipatieff[6] and Kelber [*Ber.*, **49**, 55 (1916)].

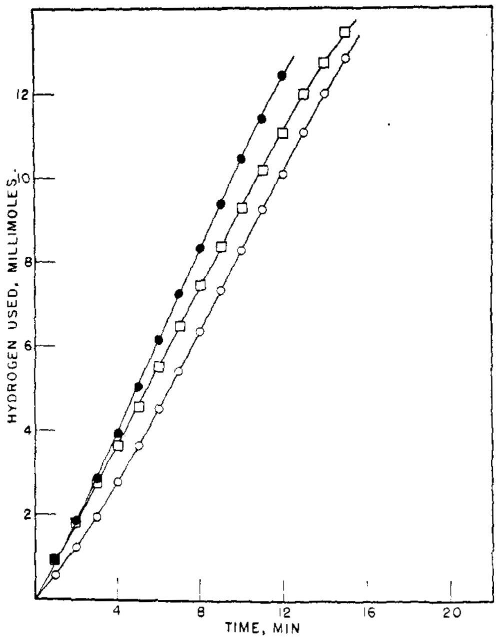

Fig. 2.—Hydrogenation of hexene-1 over Ni from $NiBr_2$: ●, raw catalyst; □, KOC_2H_5 added; ○, washed.

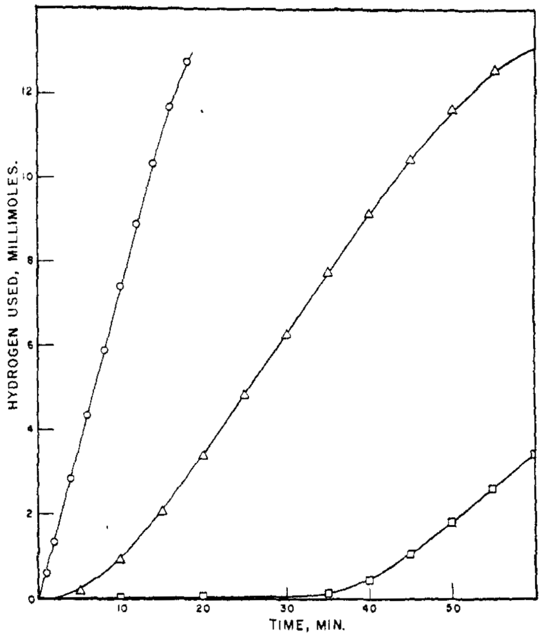

Fig. 3.—Comparative activity of nickel catalysts for the hydrogenation of allyl alcohol: □, Ni from NiO; △, Ni from $NiBr_2$; ○, W-6 Raney Ni.

Discussion

Work described in this paper and elsewhere[3] shows that the reduction of nickel(II) bromide with ammonia solutions of potassium results in the formation of elemental nickel, nickel(II) amide 2-ammonate, and one or more potassium-containing products. The latter might be expected to result from the action of potassium amide upon nickel (II) amide and/or its deammoniation products, thereby giving rise to ammonia-insoluble salts of amphoteric bases such as that described by Bohart,[15] *i.e.*, $KN(NiNK_2)_2 \cdot 6NH_3$. Data obtained by analysis of the ammonia-insoluble reduction products however fail to show a constant ratio of potassium to nitrogen and indicate that more than one such by-product is formed. The isolation of these substances presents an especially difficult problem and we have been unable either to effect a separation or to obtain X-ray diffraction patterns that might serve as a basis for identification.

The heats of activation calculated by the Arrhenius equation for hydrogenations of allyl alcohol over two independent samples of catalysts prepared in liquid ammonia are 10 and 7 kcal./mole. The surface areas of W-6 Raney nickel found in this work are somewhat higher than those found by Smith and Fuzek[16] who used data on the adsorption of palmitic acid from benzene solutions. Ammonia adsorption should lead to higher areas owing to the presence of surface less readily accessible to the larger palmitic acid molecules. Also, Ries, *et al.*,[12] reported that ammonia adsorption gave somewhat higher surface area values than nitrogen adsorption. Finally, it should be recognized that the difference between the quantity of adsorbed hydrogen found on Raney nickel in the present work (59 cc./g.) and that reported by Bougault, *et al.*,[13a] is reasonable in view of the difference in the age of the samples employed.

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[15] G. S. Bohart, *J. Phys. Chem.*, **19**, 537 (1915).

[16] H. A. Smith and J. F. Fuzek, THIS JOURNAL, **68**, 229 (1946).