[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. I. Nickel[1]

BY GEORGE W. WATT AND DARWIN D. DAVIES[2]

Burgess and Eastes[3] have described the formation of finely divided active nickel by the reduction of salts containing cationic nickel with solutions of sodium, potassium and calcium in liquid ammonia. They have recorded qualitative observations relative to the activity of such nickel as a catalyst for the conversion of alkali and alkaline earth metals to the corresponding amides. By the use of methods similar to those employed by Burgess and Eastes we have attempted to prepare nickel of optimum purity for evaluation as a hydrogenation catalyst, but have found that their work does not provide an adequate basis for the preparation of the desired catalyst in appreciable quantities. We have reëxamined the reduction of nickel(II) bromide and iodide by solutions of potassium and have given particular attention to variables that determine the purity and catalytic activity of the resulting nickel. Although the present paper is concerned primarily with the reduction reactions, preliminary experiments in which the nickel was used as a hydrogenation catalyst are described. Further experiments concerned with catalytic activity in relation to certain physical properties of the catalysts are in progress.

Experimental

Materials.—Nickel(II) bromide and nickel(II) iodide were used in the form of the corresponding 6-ammoniates which were prepared by a modification of the method of Erdmann.[4]

Anal. Calcd. for $NiBr_2\cdot 6NH_3$: Ni, 18.30; NH_3, 31.83. Found: Ni, 18.22; NH_3, 31.88.

Anal. Calcd. for $NiI_2\cdot 6NH_3$: Ni, 14.13; NH_3, 24.64. Found: Ni, 14.07; NH_3, 24.71.

Nickel(II) thiocyanate 4-ammoniate was prepared as described by Bohart.[5]

Anal. Calcd. for $Ni(SCN)\cdot 4NH$. Ni, 24.18; NH_3, 28.10. Found: Ni, 24.08; NH_3, 2 .26.

Propene-1-ol-3 was generously supplied by the Shell Chemical Corporation and was used without further purification, b. p., 95–97° (96.98[6]); $d^{20}{}_4$, 0.858 (0.852[7]). Raney nickel was prepared by the method of Covert and Adkins.[8] All other chemicals employed were of reagent grade.

Methods.—All equipment and procedures for the conduct of reactions in liquid ammonia at −33.5° in a closed system and under anhydrous conditions were substantially the same as those described by Watt and Moore.[9] Unless otherwise specified, all transfers involving products formed in liquid ammonia were made in a dry box.

All catalytic hydrogenation experiments were conducted in an apparatus of the familiar Skita type and employed approximately 0.1 g. of catalyst together with 17.5 ml. of propene-1-ol-3 (0.26 mole) in 100 ml. of 95% ethanol, with hydrogen at an initial pressure of two atmospheres.

Nickel(II) Amide 2-Ammoniate.—Burgess and Eastes[3] reported that nickel(II) amide is always formed as a by-product of the reduction of certain cationic nickel salts and it follows that this substance will be a catalyst contaminant. Since some of our preliminary data on the nitrogen content of the gross insoluble reduction products were surprisingly high, the formation and composition of the amide was reinvestigated.

In a typical experiment 0.8301 g. of nickel(II) iodide 6-ammoniate was added to a solution of the potassium amide formed from 0.1939 g. of potassium (*ca.* 25% excess) in 25 ml. of liquid ammonia. The resulting red insoluble solid was washed with liquid ammonia and dried *in vacuo* at 10^{-3} mm. for twelve hours at 25°. The product proved to be the 2-ammoniate rather than the unsolvated amide reported by Bohart[5] as the product of the interaction of nickel(II) thiocynate and potassium amide in liquid ammonia.

Anal. Calcd. for $Ni(NH_2)\cdot 2NH_3$: Ni, 47.10; N, 45.10. Found: Ni, 46.92, N, 45.32.

Identical results were obtained using nickel(II) bromide 6-ammoniate and nickel(II) thiocyanate 4-ammoniate.

Thermal Decomposition Products of Nickel(II) Amide 2-Ammoniate.—Because it was anticipated that catalysts would be subjected to different thermal treatments prior to use, it seemed necessary to determine the nature and conditions of formation of the decomposition products of the ammoniated amide.

Small samples of pure nickel(II) amide 2-ammoniate in a detachable glass bulb were heated *in vacuo* (10^{-3} mm.) under conditions such that decomposition temperatures could be determined accurately and losses in weight corresponding to volatile decomposition products (ammonia and/or nitrogen) could be measured. At 42.3° (cor.), deammoniation occurred[10] with a loss in weight amounting to 27.20% (calcd.. 27.25).

Anal. Calcd. for $Ni(NH_2)_2$: Ni, 64.70; N, 35.30. Found: Ni, 64.61; N, 35.60.

At 119.3°, the amide was converted to amorphous nickel(II) nitride[11] ($d^{25}{}_4$, 8.35) with an attendant weight loss of 24.93% (calcd. 25.00).

Anal. Calcd. for Ni_3N_2: Ni, 86.31; N, 13.69. Found: Ni, 86.20; N, 13.92.

At 362°, nickel(II) nitride was converted to nickel(I) nitride. The observed decrease in weight was 6.86% (calcd., 6.65).

Anal. Calcd. for Ni_3N: Ni, 92.63; N, 7.37. Found: Ni, 92.49; N, 7.58.

Nickel(I) nitride has been prepared by an entirely different method by Juza and Sachaze[12] who reported X-ray diffraction data and an experimental value of $d^{25}{}_4$

---

[1] This work was supported in part by grants from the University Research Institute, Project No. 25.

[2] Present address: The General Electric Co., Richland, Washington.

[3] Burgess and Eastes, THIS JOURNAL, **63**, 2674 (1941).

[4] Erdmann, *J. prakt. Chem.*, **7**, 266 (1836); **19**, 445 (1840).

[5] Bohart, *J. Phys. Chem.*, **19**, 553 (1915).

[6] Dolliver, *et al.*, THIS JOURNAL, **60**, 440 (1938).

[7] "Allyl Alcohol," Shell Chemical Corporation Technical Publication SC:46·32, Knight-Counihan Co., San Francisco, 1946, p. 42.

[8] Covert and Akkins, THIS JOURNAL, **54**, 4116 (1932).

[9] Watt and Moore, *ibid.*, **70**, 1197 (1948).

[10] This accounts for Bohart's failure to detect the diammoniate since his samples were dried at approximately 40° prior to analysis.

[11] Varied attempts to get a satisfactory X-ray diffraction pattern for this compound were largely unsuccessful; only two lines conceivably attributable to the nitride were observed. Bohart[5] described this compound as qualitatively amorphous and reported 120° as the temperature of its formation from the amide.

[12] Juza and Sachaze, *Z. anorg. allgem. Chem.*, **251**, 201 (1943).

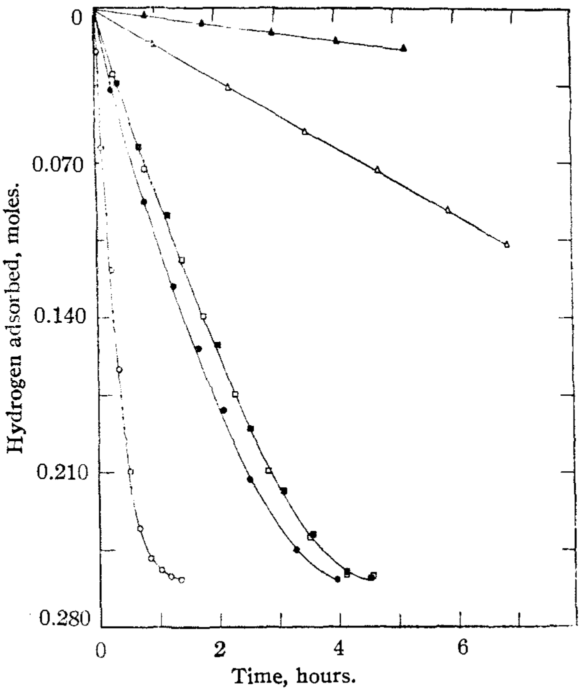

Fig. 1.—○, Raney nickel; ●, Ni from $NiBr_2$ (optimum conditions); □, Ni from $NiBr_2$ (large scale run); ■, Ni (from $NiBr_2$) heated to 130°; △, Ni from $NiBr_2$ + KI; ▲, Ni (from $NiBr_2$) heated to 365°.

7.66 as compared with a calculated value of 7.91. The density of the product formed in the present work was found to be 7.90, *i.e.*, in excellent agreement with the value calculated by Juza and Sachaze. X-Ray diffraction patterns (Cu Kα radiation) gave all of the lines reported by Juza and Sachaze and six additional lines; the corresponding interplanar spacings (d) in ångström units (relative intensities, I/I_0, in parentheses) are as follows: 1.857 (0.02), 1.769 (0.03), 1.690 (0.02), 1.648 (0.21), 1.330 (0.01, 1.161 (0.02).

Thermal decomposition of nickel (I) nitride was effected by heating samples contained in a porcelain boat in a Lindberg furnace. Decomposition occurred at 585 ± 5° (uncor.) with an attendant weight loss of 7.48% (calcd., 7.64).

Anal. Found: Ni, 99.67.

X-Ray diffraction patterns showed exclusively the lines characteristics of face-centered cubic nickel.[13]

Reduction of Nickel (II) Salts.—Typical data relative to the reduction of nickel (II) iodide and nickel (II) bromide are given in Table I. Preliminary experiments showed that, when the iodide is reduced with 2, 4 or 6 equivalents of potassium *added slowly and in small pieces*, there is considerable variation in the volumes of hydrogen evolved, large quantities of nickel(II) amide 2-ammoniate are formed, and the total nickel content of the gross insoluble product ranges from 55 to 83%. In all subsequent experiments, potassium was added as rapidly as possible. The data for Expt. 1 show that this results in a marked increase in nickel content and a decrease in the quantity of amide, while Expt. 2 reflects the increase in purity accomplished by treatment with ammonium iodide to convert the amide to nickel(II) iodide 6-ammoniate which was subsequently removed by washing. Experiments 2, 3 and 4 show the progressive decrease in purity of the nickel with increase in the K/NiI_2 ratio and the accompanying increase in amide formation. All samples of nickel from reduction of the iodide were non-pyrophoric and the X-ray diffraction patterns were characteristic of face-centered cubic nickel.

TABLE I

REDUCTION OF NICKEL(II) SALTS WITH POTASSIUM IN LIQUID AMMONIA

Expt.	Salt Formula	g.	K equiv.	H_2, cc.	Insoluble product Ni, %	N. %	K, %
1	$NiI_2\cdot 6NH_3$	0.6292	2.21	2.7	95.01	1.85	1.02
2[a]	$NiI_2\cdot 6NH_3$	1.0351	2.12	1.0	98.15	1.02	0.62
3	$NiI_2\cdot 6NH_3$	0.8086	4.02	25.6	85.05	12.20	3.05
4	$NiI_2\cdot 6NH_3$	.8551	6.01	50.2	79.85	16.35	3.81
5	$NiBr_2\cdot 6NH_3$	.9892	2.15	None	96.50	2.08	..
6[b]	$NiBr_2\cdot 6NH_3$	.9309	2.06	2.0	98.02	1.05	..
7[c]	$NiBr_2\cdot 6NH_3$	.2999	4.67	32.0	83.47	17.23	1.98
8[d]	$NiBr_2\cdot 6NH_3$	1.2248	4.88	123.0	59.79	32.50	3.03
9[e]	$NiBr_2\cdot 6NH_3$	0.9971	2.40	6.7	94.70	2.73	..
10	$NiBr_2\cdot 6NH_3$	5.0012	2.48	110.4	86.77	10.03	..

[a] Insoluble product treated with 0.550 g. of ammonium iodide. [b] Insoluble product treated with 0.5110 g. of ammonium bromide. [c] Duplication of experiment described by Burgess and Eastes.[3] [d] Nickel salt was added to solution of potassium. [e] Reduction in the presence of 0.4520 g. of potassium iodide.

The data for Expt. 5 correspond to optimum conditions for the production of pyrophoric nickel[14] of maximum purity (*i.e.*, somewhat in excess of two equivalents of potassium added rapidly), although these conditions do not ensure maximum catalytic activity unless the potassium in excess is sufficient to generate hydrogen that must be available for adsorption on the nickel. The catalytic activity of the resulting product (in comparison with Raney nickel) in the complete hydrogenation of propene-1-ol-3 is shown in Fig. 1. Although the data plotted in Fig. 1 are those from single experiments, their reproducibility is indicated by the fact that duplicate experiments which employed independently prepared catalyst samples gave substantially identical results. Shown also in Fig. 1 is the fact that this nickel is rendered almost entirely inactive when the adsorbed hydrogen is removed by heating to 365°, *i.e.*, a few degrees above the Curie point (358°). In Experiment 6, hydrogen was evolved upon addition of ammonium bromide and the nickel was non-pyrophoric and catalytically inactive. Experiment 7 represents a duplication of the typical experiment described by Burgess and Eastes[3] but our results show comparatively less nickel and more ammoniated amide in the insoluble product. Experiment 8 reflects the marked decrease in nickel content and increase in amide content that results when the nickel salt is added to the solution of potassium.

Since the nickel from the reduction of nickel(II) iodide was non-pyrophoric, this property was attributed to a selective adsorption of iodide ion which inhibited adsorption of hydrogen. Accordingly, in Expt. 9, nickel(II) *bromide* was reduced in the presence of a quantity of potassium iodide sufficient to provide an iodide ion concentration equivalent to that prevailing in corresponding reductions of nickel(II) iodide. The product was non-pyrophoric and the relative catalytic inactivity is shown in Fig. 1.

Experiment 10 shows the decrease in nickel content that results from attempts to prepare the catalyst on a relatively larger scale. Similar results were obtained in experiments employing approximately 7.5 and 10 g. of nickel(II) bromide. Figure 1 shows that the decreased purity of the catalyst does not decrease catalytic activity greatly and that substantially the same degree of activity is observed when the same product is heated to a temperature (130° at 10^{-3} mm.) insufficient to remove adsorbed hydrogen but sufficient to convert nickel(II) amide 2-ammoniate to nickel(II) nitride.

With reference to the adsorption of hydrogen by nickel produced as described above, we have confirmed directly Burgess and Eastes' statements to the effect that part or

---

(13) Hanawalt, Rinn and Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

(14) This product, like the non-pyrophoric product from nickel(II) iodide, consisted of face-centered cubic nickel.

all of the adsorbed hydrogen is released upon treatment with ammonium salts in liquid ammonia. By experiments of which the following is typical, we have also confirmed indirectly their statement that as much as 100 cc. of hydrogen/g. nickel may be adsorbed. Thus, in a case similar to Expt. 10, analyses showed a total nickel content of 86.68% and 10.10% nitrogen. If it is assumed that all of the nitrogen is present as nickel(II) amide 2-ammoniate, that this compound will decompose thermally as described earlier in this paper, and that hydrogen is present in the quantity specified by Burgess and Eastes, then a 0.2858-g. sample heated above 358° should evolve 38.7 cc. of ammonia, 21.8 cc. of hydrogen, and 1.9 cc. of nitrogen. The volumes of these gases found experimentally were 37.2, 20.9 and 2.7, respectively.

Summary

1. The action of potassium amide in liquid ammonia at −33.5° upon cationic nickel salts yields nickel(II) amide 2-ammoniate.

2. Thermal decomposition of nickel(II) amide 2-ammoniate at 10^{-3} mm. produces successively: nickel(II) amide (at 42.3°), nickel(II) nitride (at 119.3°), nickel(I) nitride (at 362°), and elemental nickel and nitrogen (at 585°).

3. The reduction of nickel(II) bromide and iodide by solutions of potassium in liquid ammonia at −33.5° yields, respectively, pyrophoric and non-pyrophoric nickel together with some nickel (II) amide 2-ammoniate. Conditions required to minimize formation of the latter are described.

4. Preliminary experiments on the catalytic activity of nickel from the reduction of nickel salts in ammonia in the hydrogenation of propene-1-ol-3 are described.

AUSTIN, TEXAS RECEIVED MARCH 12, 1948

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Measurement of the Diffusion Coefficient of Hydrogen Peroxide Vapor into Air

BY R. L. MCMURTRIE AND F. G. KEYES

I. Introduction

The measurement of hydrogen peroxide vapor diffusion is complicated, in common with the measurement of other physical properties, by the unavoidable decomposition of peroxide in contact with any known surface. Among the methods available for the measurement of gaseous diffusion, the only one which appears applicable to peroxide measurements is a method first developed by Stefan[1] in which diffusion takes place unidirectionally at constant rate from a source of saturated vapor to a point of low vapor concentration.

An apparatus has been developed for the application of this method to peroxide diffusion and measurements made of the diffusion rate of peroxide vapor into air.

II. Method

The method used is a basically simple one originally developed by Stefan[1] applicable where one of the diffusing components is a liquid at ordinary temperatures. Diffusion takes place through a stagnant gas in a glass tube; liquid at the bottom of the tube provides vapor of a fixed known concentration, while at the top of the tube zero concentration of vapor is effected by conducting a stream of the second gas across the end of the tube. The rate of diffusion is determined from the observed loss of liquid with time. One thus has a case of steady unidirectional diffusion of one gas through a second stagnant gas, under a fixed concentration gradient. Under these conditions the fundamental differential expression for diffusion becomes

$$\Gamma = -Dn/n_2 \, \partial n_1/\partial x \qquad (1)$$

Gamma is the diffusion rate, g. moles per sq. cm. per second, D the diffusion coefficient, and n_1 the concentration of the diffusing gas, in gram moles per cc. Integrating between limits x from 0 to L, n_1 from n_{10} to 0, we find

$$\Gamma = Dn/L \ln (1 - n_{10}/n) \qquad (2)$$

where x is measured from the liquid surface above which the concentration of the diffusing gas is n_{10}; n_2 is the concentration of stagnant gas; and n is the total concentration.

In the case of peroxide diffusion the situation is complicated by the simultaneous diffusion of the oxygen evolved by the slowly decomposing liquid peroxide. For this case of diffusion of two gases through a third stagnant gas, the following differential equations apply

$$-\partial n_1/\partial x = \Gamma_1 n_2/D_{12} - \Gamma_2 n_1/D_{12} + \Gamma_1 n_3/D_{13} \qquad (3)$$

$$-\partial n_2/\partial x = \Gamma_2 n_1/D_{12} - \Gamma_1 n_2/D_{12} + \Gamma_2 n_3/D_{13} \qquad (4)$$

where subscripts 1 and 2 refer to the first and second diffusing gases, and n to the total concentration.

A solution of these equations in the form of two simultaneous equations has been obtained.[2]

$$\Gamma_1/D_{13} + \Gamma_2/D_{23} = n/L \ln n/n_{30} \qquad (5)$$

$$\Gamma_1 + \Gamma_2 = D_{12}n/L \ln \frac{n(1/D_{13} - 1/D_{23})}{n(1/D_{13} - 1/D_{23}) + n_{20}\,(\Gamma_1 + \Gamma_2)/\,\Gamma_2(1/D_{12} - 1/D_{13}) - n_{10}(\Gamma_1 + \Gamma_2)/(\Gamma_1(1/D_{12} - 1/D_{13})} \qquad (6)$$

For small concentrations of the diffusing substances the results are but little different from

---

[1] Stefan, *Sitz. Akad. Wiss. Wien.*, Abt. II, **62**, 388 (1870); *Ann. Physik*, **41**, 723 (1890).

[2] Sherwood, "Absorption and Extraction," McGraw-Hill Book Co., New York, N. Y., 1937.