

Hydrogenolysis of Hydrazine over Metals

KEN-ICHI AIKA, TOMOHISA OHHATA, AND ATSUMU OZAKI

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo, Japan*

Received January 26, 1970

Decomposition and hydrogenolysis of hydrazine over metals have been studied by means of micro-catalytic gas chromatographic technique near 200°C. The decomposition of hydrazine over metals in helium is represented as $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$. Some part of hydrazine is hydrogenated to ammonia in hydrogen carrier. A regularity is observed in the selectivities of metals in the hydrogenolysis, that is, the selectivity to ammonia increases with decrease in the parameter $-\Delta H_0^\ddagger$ which has been proposed from previous work for the adsorption of gases over metals. The mechanism of decomposition and hydrogenolysis of hydrazine over metals is discussed.

INTRODUCTION

The decomposition of hydrazine has been investigated in the gas phase and/or in liquid phase by a number of workers (1-5). Very few of those workers, however, deal with the hydrogenolysis of hydrazine, which seems to be interesting in relation to the mechanism of ammonia synthesis. One possible reason for such a circumstance might be the difficulty in handling hydrazine. Indeed, it has a low vapor pressure at ambient temperature and is apt to decompose. Quantitative determination of hydrazine is another problem.

Such a difficulty has been overcome in this study by adopting the micro-catalytic gas chromatographic technique (6) giving attention to the selectivity of hydrogenolysis. This procedure has made it possible to study the characteristic feature of various metals in the hydrogenolysis of hydrazine. No such work has been done before.

EXPERIMENTAL METHODS

1. Procedure

Reactions were performed by means of the micro-catalytic gas chromatographic technique, using two detectors and three columns in series. The flow diagram is shown in Fig. 1. Either helium or hydrogen

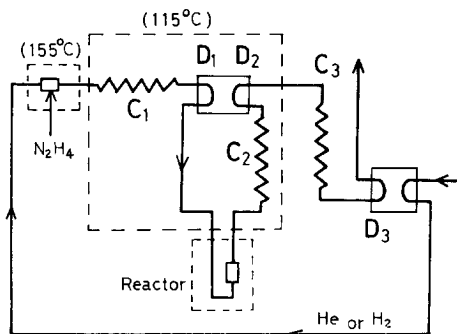


FIG. 1. Micro-catalytic gas chromatographic apparatus; C, column; D, detector.

was used as the carrier gas. Liquid hydrazine was fed as pulses of 2 to 4 μl by means of a micro syringe through a septum. The sample pulse was, after evaporation, subjected to separation of a trace of water involved in the sample by the column C_1 and then the amount of pure hydrazine was determined by the detector D_1 . The reaction products in the effluent from the reactor were separated in two steps, first by the column C_2 into $(\text{N}_2 + \text{NH}_3)$ and N_2H_4 and second by the column C_3 into N_2 and others. The flow line was made of glass tubing and partly heated to avoid condensation of hydrazine. The column materials used were as follows:

Column	Packing	Length (cm)	Temp (°C)
C ₁	Polapack (Type Q)	15	115
C ₂	Polapack (Type Q)	30	115
C ₃	Silica gel	50	25
	+ Molecular sieve	60	25

A typical chromatogram is shown in Fig. 2.

Polyethylene glycol (7) and dinonyl phthalate + triethanolamine (8) were also tested but gave unsatisfactory separation of hydrazine from ammonia.

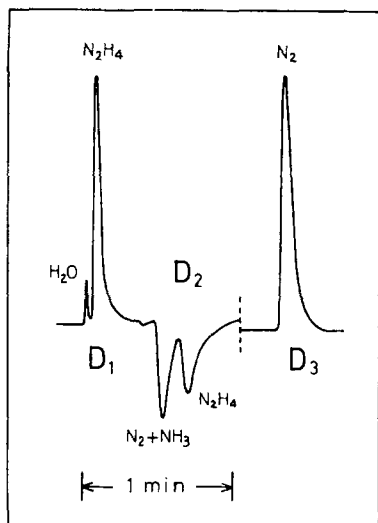


FIG. 2. A typical chromatogram for the hydrogenolysis of hydrazine.

2. Catalysts

Some catalysts (Ir, Ru, Pt, Ni, Co, Rh) were prepared by impregnating Celite or kieselguhr with aqueous solution of metal salt followed by drying at 120°C, and baking at 400°C. The metal content in these catalysts was held at 3–5% wt.

Some catalysts were prepared by tabletting oxide powder (Fe, W) or commercial metal powder (Mo). Molybdenum nitride was obtained by nitriding molybdenum metal with nitrogen at 502°C. The others were singly promoted (Al₂O₃, 2.2%) and doubly promoted (Al₂O₃, 3.7%; K₂O, 1.1%; CaO, 1.0%) iron catalysts for ammonia synthesis obtained from the Government Chemical Industrial Research Institute, Tokyo.

All these catalysts were pretreated *in situ* with flowing hydrogen at 400°C for several hours.

3. Reagents

Anhydrous hydrazine was prepared by distillation of hydrazine hydrate in the presence of barium oxide under a reduced hydrogen pressure (9). The distilled hydrazine still contained about 1% water. Both hydrogen and helium used for carrier gas were purified by passing through a platinum catalyst column at 350°C followed by drying by a liquid nitrogen trap.

RESULTS AND DISCUSSION

1. Decomposition of Hydrazine

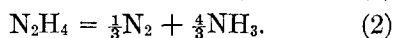
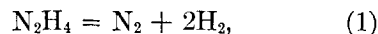
The selectivity of metals for the decomposition of hydrazine was examined by using helium as the carrier gas. The decomposition became appreciable at about 150°C over most metals tested and reached 100% conversion at around 250°C, although the data of conversion showed a poor reproducibility even at a fixed temperature. The decomposition products found were ammonia and nitrogen, and no hydrogen was detected.

The selectivity of the decomposition defined by

$$S = 100 \times [\text{NH}_3] / (2[\text{N}_2] + [\text{NH}_3])$$

is calculated from the amount of ammonia and nitrogen, and is shown in Table 1 for metals. In spite of the poor reproducibility in the conversion, the selectivity values of catalysts were reproducible and hardly affected by the reaction temperature.

The following two typical reactions may be considered to take place in the decomposition of hydrazine (2):



From a thermodynamic standpoint, the reaction (1) is fully possible under the reaction condition of 1 atm and 200°C. But no hydrogen was detected in the product. This result indicates that the decomposition of hydrazine in helium is represented by

Eq. (2). If this is the case, the selectivity S should remain at 66.7%. The observed values over metals as shown in Table 1 are not so different from the expected value, but always a little higher, and range from 68 to 72%. This deviation from the expected value may be due to irreversible adsorption of hydrogen-deficient species such as N_2H_2 or NH as pointed out by Frolov (4).

TABLE 1
THE SELECTIVITY OF METALS FOR THE
DECOMPOSITION OF HYDRAZINE

Carrier gas, He; flow rate, 36.3 ml/min;
 $S = \frac{[NH_3] \times 100}{2[N_2] + [NH_3]}$

Catalyst	Temp (°C)	S
Ir	133	71.9
	213	71.2
W	195	68.0
	275	68.8
Fe	245	67.3
Fe(Al,K)	247	69.1
Ni	233	72.6
Ru	177	68.9
	227	68.8
Pt	201	69.8
	240	68.2

The stoichiometry of Eq. (2) suggests that the decomposition of hydrazine proceeds via an intermediate, favorable for the formation of ammonia, e.g., NH_2 . Indeed the dissociation energy of the N-N bond in hydrazine [ca. 60 kcal (10)] is much less than that of the N-H bond [at least 83 kcal (2)], and thus the homogeneous decomposition of hydrazine has been believed to proceed via the NH_2 intermediate (10). In this respect, it seems likely that the hydrazine molecule is dissociated into NH_2 rather than into N-N and H, thus resulting in the observed absence of hydrogen formation. If this is the case, the amino radical would react with hydrazine to form ammonia leaving a precursor of nitrogen.

2. Hydrogenolysis of Hydrazine

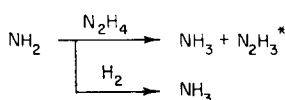
Hydrogenolysis of hydrazine was performed in the hydrogen carrier gas over

TABLE 2
THE SELECTIVITY OF METALS FOR THE
HYDROGENOLYSIS OF HYDRAZINE
Carrier gas, H_2 ; flow rate, 75 ml/min;
 $S = \frac{[NH_3] \times 100}{2[N_2] + [NH_3]}$

Catalyst	Temp (°C)	S
Pt	182	87.9
	240	87.7
Ir	203	85.0
	258	87.1
Ru	175	82.4
	219	85.1
Rh	180	83.0
	223	84.2
Fe(Al,K)	217	80.9
	233	81.9
Ni	177	78.8
	267	79.4
Fe	195	77.1
	210	77.4
Co	182	76.5
	210	76.2
Fe(Al)	243	78.4
	253	75.4
Mo	185	72.2
	240	74.5
W	160	72.2
	200	74.2
Mo_2N	160	70.2
	205	72.2

metals, and the results are shown in Table 2 as the selectivity S . As clearly shown in Table 2, the selectivity is generally higher than that in helium. This means that the hydrogenolysis of hydrazine really takes place. In the case of platinum metal which gives the highest selectivity, a larger part of the nitrogen formed in the helium carrier is now converted to ammonia in the hydrogen carrier.

Since the adsorption of nitrogen-containing species over metals would be stronger than that of hydrogen, the initial step of the hydrogenolysis seems to be identical with that of the simple decomposition. Thus the selectivity seems to depend on the relative ease of NH_2 to react with hydrogen. That is,



In Fig. 3, the selectivities observed over metals are plotted against the heat of for-

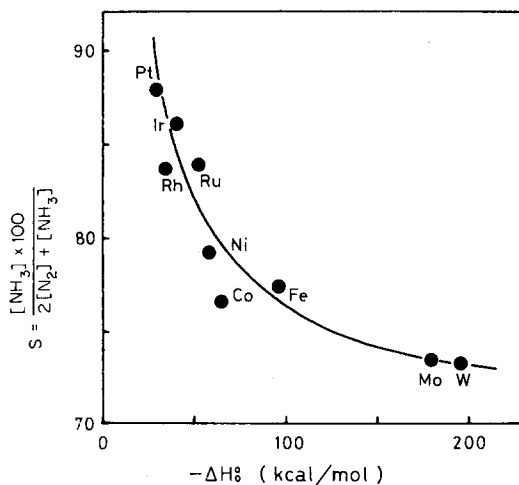


FIG. 3. Plot of the selectivity of metals (S) versus the heat of formation of the metal oxide of the highest oxidation state per gram atom of metal ($-\Delta H_0^3$).

mation of the metal oxide of the highest oxidation state per gram atom of metal ($-\Delta H_0^3$), which has been accepted as a parameter of adsorption strength of metals (11). As shown, the selectivity monotonously decreases with increase in $-\Delta H_0^3$. This result would be reasonable on the ground of the scheme assumed above, because $-\Delta H_0^3$ may be considered a parameter of hydrogenation activity of metals as previously shown for the hydrogenation of ethylene, where the activity decreases with increase in $-\Delta H_0^3$ (12). Thus it may be concluded that the selectivity observed here is indicative of the relative effectiveness of metals in the hydrogenation of NH_2 .

3. Relevance to the Ammonia Synthesis

It has been known that only those metals of medium value of $-\Delta H_0^3$ such as iron

can be good catalysts for the ammonia synthesis reaction (13); whereas the lower the $-\Delta H_0^3$, the higher the selectivity observed here. This difference reflects the difference in the key steps. The rate of ammonia synthesis is determined by the step of dissociation of the $\text{N}\equiv\text{N}$ bond (13), whereas the selectivity is determined by the step of hydrogenation of adsorbed NH_2 . It was previously shown that the potash promoter in the iron catalyst changes the main adsorbed species from N over the unpromoted iron to NH over the doubly promoted catalyst (14). In this connection, note that the selectivity over the doubly promoted catalyst is clearly higher than that over the singly promoted or unpromoted iron. This result would be reasonable if potash determines the main adsorbed species.

REFERENCES

1. ASKEY, P. J., *J. Amer. Chem. Soc.* **52**, 970 (1930).
2. AUDRIETH, L. F., AND OGG, B. A., "The Chemistry of Hydrazine," Wiley, New York, 1951.
3. KEIER, N. P., "Proceedings of the 3rd International Congress on Catalysis" (W. M. H. Sachtler, G. C. A. Schuit, and P. Zwietering, eds.), p. 1021. North-Holland, Amsterdam, 1964.
4. FROLOV, V. M., *Kinet. Katal.* **6**, 149 (1965).
5. VÖLTER, V. J., AND LIETZ, G., *Z. Anorg. Allg. Chem.* **366**, 191 (1969).
6. KOKES, R. J., TOBIN, H., JR., AND EMMETT, P. H., *J. Amer. Chem. Soc.* **77**, 5860 (1955).
7. CAIN, E. F. C., AND STEVENS, M. R., "Gas Chromatography" (H. J. Noebels, R. F. Wall, and N. Brenner, eds.), p. 343. Academic Press, New York, 1961.
8. PRÖSCH, U., AND ZÖPFL, H. J., *Z. Chem.* **3**, 468 (1963).
9. HALE, C. F., AND SHETTERLY, F. F., *J. Amer. Chem. Soc.* **33**, 1071 (1911).
10. JOLLY, W. L., "The Inorganic Chemistry of Nitrogen," p. 65. Benjamin, New York, 1964.
11. TANAKA, K., AND TAMARU, K., *J. Catal.* **2**, 366 (1963).
12. TANAKA, K., AND TAMARU, K., *Kinet. Katal.* **7**, 242 (1966).
13. AIKA, K., AND OZAKI, A., *J. Catal.* **16**, 97 (1970).
14. AIKA, K., AND OZAKI, A., *J. Catal.* **13**, 232 (1969).

* Subsequent reaction of N_2H_3 would be

