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NOTES

The Catalytic Decomposition of Nitrogen-15-Labeled Hydrazine on MgO-Supported Iron

The heterogeneous decomposition of hydrazine is catalyzed by several metals (*1–3*). As in the ammonia synthesis, iron and osmium are favorable catalysts (*4*). During the decomposition, two reactions have been observed, namely, the formation of molecular nitrogen and hydrogen,

$$N_2H_4 \rightarrow N_2 + 2H_2, \qquad (1)$$

and the formation of ammonia,

$$3N_2H_4 \rightarrow 4NH_3 + N_2. \qquad (2)$$

The extent of reactions (1) or (2) depends on the presence of hydrogen, since an additional reaction, the hydrogenolysis (*5*) of hydrazine,

$$N_2H_4 + H_2 \rightarrow 2NH_3, \qquad (3)$$

also competes.

If N_2H_4 is considered to be a partially hydrogenated molecule with a hydrogen saturation between N_2 and NH_3, reactions (1) and (3) have opposite influence on the extent of hydrogen saturation of nitrogen. Reaction (1) dehydrogenates N_2H_4 to molecular nitrogen, reaction (3) hydrogenates N_2H_4 to ammonia and reaction (2) involves both processes. Since the yield of ammonia increases with the hydrogen pressure, reactions (1), (2) and (3) are not independent.

For reaction (1), NH_2-surface species have been assumed by several authors (*2, 6*) on different catalysts because of the low bond energy of the N–N bond ($\approx$60 kcal/mol) compared with that of the N–H bond (83 kcal/mol) in hydrazine. According to this assumption, surface amids and -imids are hydrogenated to ammonia or dehydrogenated to "surface nitrids" which decompose into molecular nitrogen. The purpose of this contribution is to elucidate the reaction mechanism from results obtained by using isotopically labeled molecules.

The steady-state condition of N_2H_4 decomposition involves all stoichiometric reaction steps of the ammonia synthesis. However, no comparison can be made for the Polanyi energy surfaces of both reactions. The reverse direction of the dehydrogenation of N_2H_4 may be formulated as:

$$N_2 \rightleftharpoons 2N, \qquad (4a)$$
$$2N + H_2 \rightleftharpoons 2NH, \qquad (4b)$$
$$2NH + H_2 \rightleftharpoons 2NH_2, \qquad (4c)$$
$$2NH_2 \rightleftharpoons N_2H_4, \qquad (4d)$$

and the subsequent hydrogenation as:

$$N_2H_4 \rightleftharpoons 2NH_2, \qquad (4e)$$
$$2NH_2 + H_2 \rightleftharpoons 2NH_3. \qquad (4f)$$

Since Eqs. (4d) and (4e) cancel, the sum in Eqs. (4a)–(4f) describes intermediate steps of the ammonia synthesis assuming the dissociative chemisorption of nitrogen.

The hypothesis of hydrogenation of nondissociated nitrogen leads to the reaction scheme (5d to 5f), which is similar to the mechanism of the ammonia synthesis as derived by Brill (*7*).

$$N_2 + H \rightleftharpoons N_2H, \qquad (5a)$$
$$\vdots$$
$$N_2H_3 + H \rightleftharpoons N_2H_4 \qquad (5d)$$
$$\vdots$$
$$N_2H_5 + H \rightleftharpoons 2NH_3 \qquad (5f)$$

Since the nitrogen bond does not dissociate, the two individual nitrogen atoms in the N_2 molecule are exactly the same as in

N_2H_4. If this reaction scheme applies, the decomposition of a mixture of $^{15}N^{15}NH_4$ and $^{14}N^{14}NH_4$ should not yield any isotope mixture, i.e., $^{14}N^{15}N$ should be absent in the product molecular nitrogen.

To test which reaction scheme (4a–f) or (5a–f) applies, iron catalysts on a MgO support were prepared from the same charge and by exactly the same procedure as described by Brill, Jírû and Schulz (*8*). The catalyst was placed in a flow reactor and reduced *in situ* for 20 hr at 410°C with hydrogen ($P_{H_2} \approx 1$ atm) prior to catalytic experiments. The hydrazine samples ^{14}N-$^{14}NH_4$ with naturally occurring isotopic distribution were prepared by the method of Bock (*9*). Heavy hydrazine $^{15}N^{15}NH_4$ was prepared by VEB Berlin-Chemie and contained traces of H_2O. Hydrogen was cleaned by diffusion through palladium.

The reaction chamber was part of a UHV gas inlet system of an Inghram type mass spectrometer (60° magnetic sector field) which was simultaneously used for field ion studies of hydrazine. Approximately 1 cm^3 of the catalyst was carried by a fritted glass holder within a 10 mm glass tube heated by an electrical furnace. Hydrazine was decomposed at 5 Torr partial pressure with a small flow rate and a preferentially high conversion. Since no rate measurements were made, diffusion-controlled rate processes are not important. Part of the product was analyzed mass spectrometrically. The behavior of hydrazine during field ionization and the analysis of the decomposition products are reported elsewhere (*10*). Analytical results reported in this contribution were made using a Finnigan type 400 residual gas analyzer.

Measurements of the decomposition reaction were carried out at 26 and 365°C. The upper temperature limit was selected in order to achieve a high conversion without an excessive NH_3 decomposition. Between the experiments with different isotope mixtures, the reaction vessel was evacuated. During the mass spectrometric analysis one has to take care of two phenomena, namely, the memory effect, which is caused by the adsorption and exchange of previously introduced samples, and fragmentation. The fragmentation of $N_2H_4^+$ ions yields also those ions which are expected from the catalytic reaction products NH_3, N_2 and H_2. Mass spectra of pure undecomposed samples were taken for elimination of fragment intensities.

For the statistical isotopic distribution of nitrogen,

$$^{14}N^{14}N + {}^{15}N^{15}N \rightleftharpoons 2\,{}^{14}N^{15}N, \qquad (6)$$

the equilibrium constant K_{eq} is 4, if differences in zero point energies are neglected. Accordingly, the statistical distribution of molecular weights M30, M29 and M28 as function of the total content of $^{15}N\%$, γ, is represented in Fig. 1 (top).

Experimental values for the isotopic distribution of nitrogen are given for different isotopic mixtures of decomposing hydrazine in Table 1. For calculating partial pressures of reaction products from mass spectrometric ion intensities, the fragmentation of molecular ions was taken into account and the ionization efficiencies were evaluated.

As seen in Fig. 1 (bottom), the experimental isotopic distribution is much less than statistical expectations. Most of the experiments yield a value which exactly

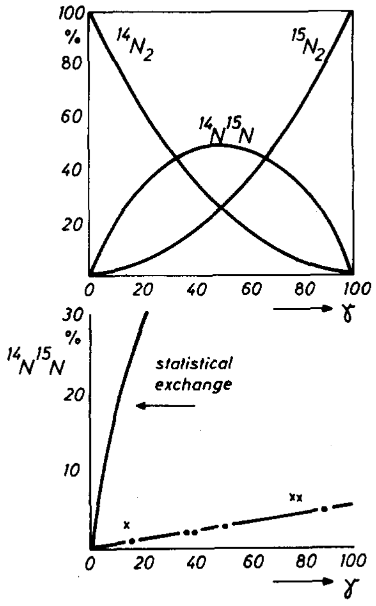

FIG. 1. Statistical and experimental isotope distribution $^{15}N_2 + {}^{14}N_2 = 2\,{}^{14}N^{15}N$.

TABLE 1
EXPERIMENTAL ISOTOPE DISTRIBUTION $^{15}N_2H_4 + {}^{14}N_2H_4 \rightarrow {}^{15}N_2 + {}^{14}N_2 + {}^{14}N^{15}N$

Expt no.	T (°C)	γ	$^{14}N_2$ m/e 28	$^{14}N^{15}N$ m/e 29	$^{15}N_2$ m/e 30
3	350	15.5	84.2	0.6	15.2
5	365	39.5	59.6	1.9	38.5
9	350	46.3	51.3	2.4	46.3
10	300	55.5	43.1	2.8	54.1
11	265	13.7	84.8	3.1	12.1
13	200	37.7	61.2	2.1	36.7
14	26	89.1	8.5	4.8	86.7
16	145	79.7	16.9	6.7	76.4
17	242	79.2	17.2	7.2	75.6

confirms the 5.1% $^{14}N^{15}NH_4$ contamination of the $^{15}N_2H_4$ sample. Three of the experiments show deviations to higher $^{15}N^{14}NH_4$ concentrations. However, these results are still more than an order of magnitude less than for statistical distributions. Since the extent of reactions (1) and (2) changes with reaction temperatures and hydrogen pressures, the partial pressure of ammonia differs for different experiments. The increase in $^{14}N^{15}N$ partial pressure seems to increase with the partial pressure in ammonia. Further experiments have to be made in order to evaluate details of this reaction mechanism.

Thus, surface amids, -imids and -nitrids are not formed as intermediates on the reaction path from hydrazine towards molecular nitrogen and hydrogen. The results also demonstrate that a reaction mechanism as formulated in Eq. (5) may be possible.

This result therefore abrogates one of the major arguments against the mechanism of molecular nitrogen hydrogenation. Contrary to formulations used in the literature (*6*) the relatively weaker N–N bond of the hydrazine molecule remains stable during the decomposition. This is in agreement with the general lack of correlations between bond strength and catalytic reactivity. The H/D-isotope exchange of hydrocarbons in most cases exceeds isomerization reactions although the C–H bond is stronger than the C–C bond.

Finally, thermodynamic equilibrium constants of individual steps of reactions (4) and (5) have to be considered. At room temperature and normal pressure the log K_p-values are +3,4 for the ammonia synthesis and −27.8 for the hydrazine formation (K_p in atm).

Therefore, the hydrazine decomposition studied in this investigation may proceed on a different Polanyi energy-surface than the ammonia synthesis.

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