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Catalytic Decomposition of ^{15}N-Labeled Hydrazine on Alumina-Supported Metals

The catalytic decomposition of hydrazine has been thoroughly investigated (*1–15*) but the mechanism of this reaction is not clearly understood. The formation of the products can be accounted for by the following reactions (*1*).

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad (1)$$

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

The selectivity of the catalysts, Y, is taken as the decomposition percentage according to reaction (1) and is calculated from the amount of hydrogen and nitrogen:

$$\frac{[H_2]}{2(3[N_2] - [H_2])} \cdot 100.$$

The activities and selectivities of most of Group VIII and I$_B$ metals, deposited on a low-area α-alumina, have been measured previously, in a flow reactor (*16*). The selectivities are the highest and sometimes are close to 100% on three metals, namely, Rh, Pd, and Pt. On all other metals as well as on the alumina support alone, hydrazine decomposes mainly through reaction (2) above, and Y is always less than 10%. Furthermore, the selectivities do not vary significantly with N_2, H_2, or NH_3 pressures but do strongly depend on temperature. The secondary reactions of synthesis and decomposition of ammonia do not occur to a significant extent below 300°C on any of the catalysts used. This suggests that the changes in selectivities can result from changes in mechanism according to the nature of the metal and the temperature range.

The various mechanisms put forward up to now generally involve an N–N bond breaking step followed by a recombination of adsorbed N atoms, and consequently nitrogen scrambling is to be expected. On the contrary, in the trimolecular mechanisms postulated by Szwarc (*1*), both nitrogen atoms in the N_2 molecule come from the same N_2H_4 molecule. It is thus of interest to check a possible redistribution of N by using ^{15}N label and, more precisely, by studying the decomposition of mixtures of normal and ^{15}N-labeled hydrazine. For example, if there were no randomization at all the decomposition of an equimolar mixture of $^{14}N_2H_4$ and $^{15}N_2H_4$ should give an equimolar mixture of $^{14}N_2$ and $^{15}N_2$, whereas a complete randomization should lead to the following distribution:

$$[^{14}N_2] = 25\%;$$
$$[^{15}N_2] = 25\%;$$
$$[^{14}N^{15}N] = 50\%.$$

Previous ^{15}N-labeled hydrazine decomposition investigations reveal a lack of scrambling in some cases, namely, on supported rhodium in the liquid phase (*10*), on supported iron in the gas phase (*17*), and even in thermal decomposition in a quartz or glass vessel (*18*). Conversely, scrambling was observed during hydrazine oxidation (*10, 19, 20*). It was therefore

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interesting to study ^{15}N-labeled hydrazine decomposition on the whole series of catalysts the selectivities of which had been measured previously.

For practical reasons (small amount of ^{15}N-labeled hydrazine available, difficult analysis of the gases from the flow reactor), the catalytic decomposition was now carried out in a static reactor in which the gases were recirculated through the catalyst by a Pyrex pump. In fact hydrazine was only partially labeled and the isotope atom fraction, γ, was measured as 0.468 ± 0.007 (in normal hydrazine, $\gamma_o = 0.0038$) and was statistically distributed between the different forms of hydrazine:

$$\frac{[^{14}N^{15}NH_4]^2}{[^{14}N_2H_4]\cdot[^{15}N_2H_4]} = 4.$$

The enriched hydrazine, purified to less than 2% (w/w) water, was prepared from ^{15}N-enriched hydrazinium sulfate (purchased from Isocommerz GmbH, Berlin-Buch, Germany) by exchange with liquid ammonia. After being diluted once or twice with normal hydrazine, the sample was vaporized into the reactor ($p_{N_2H_4} \simeq 30$ Torr) with Argon ($p_{Ar} \simeq 50$ Torr). After the decomposition monitored by a squalane manometer had reached completion, ammonia and traces of N_2H_4 were condensed in a liquid air trap and the remaining H_2, N_2, and Ar were pumped out by a Toepler pump. The ratio H_2/N_2 was measured by vpc and N_2 was analyzed by mass spectrometry (mass numbers 28, 29, 30). The rate of dilution of labeled hydrazine was checked by the same measurement:

$$d = \frac{[^*N_2H_4]}{[^*N_2H_4] + [^nN_2H_4]}.$$

If no scrambling occurs the mass peak height ratios, $p = M(30)/M(28)$ and $q = M(29)/M(28)$, will be calculated respectively by the following formulae:

$$p = \frac{d\gamma^2 + (1-d)\gamma_o^2}{d(1-\gamma)^2 + (1-d)(1-\gamma_o)^2},$$

$$q = 2\,\frac{d\gamma(1-\gamma) + (1-d)\gamma_o(1-\gamma_o)}{d(1-\gamma)^2 + (1-d)(1-\gamma_o)^2}.$$

On the other hand, in the case of complete scrambling, one obtains:

$$p = \frac{[d\gamma + (1-d)\gamma_o]^2}{[d(1-\gamma) + (1-d)(1-\gamma_o)]^2},$$

$$q = 2\,\frac{[d\gamma + (1-d)\gamma_o][d(1-\gamma) + (1-d)(1-\gamma_o)]}{[d(1-\gamma) + (1-d)(1-\gamma_o)]^2}.$$

The p and q values deduced from mass spectral data are given in Table 1 for the various metals and are to be compared with the two calculated values.

The results clearly show that in all cases p and q values agree, within the limit of experimental error, with a complete lack of scrambling since the isotopic distribution in nitrogen is always the same as in the starting hydrazine whatever the experimental conditions may be.

Thus, in the catalytic decomposition of N_2H_4 on metals, in the temperature range 60–300°C, nitrogen is always formed from a single hydrazine molecule without any N–N bond breaking and N scrambling. Consequently, if the changes in selectivity under the influence of temperature or from one metal to another can be associated with changes in reaction paths, the actual mechanisms never give rise to a redistribution of N atoms. This result is perhaps attributable to the fact that none of the actual mechanisms involve an N–N bond

TABLE 1

Isotopic Distribution According to $^{14}N_2H_4 + {}^{15}N_2H_4 + {}^{14}N^{15}NH_4 \rightarrow {}^{14}N_2 + {}^{15}N_2 + {}^{14}N^{15}N$

Metal (wt%/ α-alumina)	Metal weight (mg)	T (°C)	Y^a (%)	d^a	^{15}N atom fraction in N_2	p and q values[a]		
						Measured	Calculated	
							Without scrambling	With scrambling
Ru (0.5%)	7.5	80	0.45	0.356	0.169 ± 0.007	$p = 0.102 \pm 0.007$	0.105	0.040
						$q = 0.249 \pm 0.006$	0.243	0.405
Co (5%)	50	160	0.66	0.571	0.269 ± 0.005	$p = 0.217 \pm 0.005$	0.213	0.134
						$q = 0.476 \pm 0.017$	0.487	0.734
Rh (0.5%)	2.5	65	33	0.386	0.183 ± 0.003	$p = 0.121 \pm 0.003$	0.118	0.049
						$q = 0.267 \pm 0.010$	0.271	0.446
Ir (0.5%)	2.5	65	0.25	0.497	0.235 ± 0.005	$p = 0.173 \pm 0.007$	0.171	0.093
						$q = 0.391 \pm 0.007$	0.391	0.613
Ni (5%)	50	190	1.20	0.488	0.230 ± 0.005	$p = 0.166 \pm 0.006$	0.165	0.088
						$q = 0.370 \pm 0.017$	0.378	0.596
Pd (5%)	50	110	33	0.365	0.173 ± 0.004	$p = 0.119 \pm 0.005$	0.109	0.042
						$q = 0.266 \pm 0.010$	0.250	0.417
Pt (1%)	10	90	10	0.513	0.242 ± 0.001	$p = 0.182 \pm 0.002$	0.179	0.100
						$q = 0.403 \pm 0.005$	0.410	0.639
Cu (5%)	75	210	0.61	0.250	0.120 ± 0.003	$p = 0.070 \pm 0.003$	0.067	0.018
						$q = 0.160 \pm 0.005$	0.156	0.272
Empty reactor		310	1.50	0.395	0.187 ± 0.007	$p = 0.120 \pm 0.006$	0.121	0.051
						$q = 0.282 \pm 0.015$	0.279	0.459

[a] See text for definitions.

breaking, but, perhaps, it is also simply associated with a lack of mobility of the reaction intermediates such as NH_2, NH, or N, this surface mobility being necessary for scrambling to occur.

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R. Maurel
J. C. Menezo

Groupe de Recherches sur la Catalyse en Chimie Organique Equipe de Recherche Associée au CNRS
Université de Poitiers
40, Avenue du Recteur Pineau
86022 Poitiers, France

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