Investigations on the Rupture of the N-N-Bond within the Anodic Oxidation and Catalytic Decomposition of Hydrazine

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Mass spectrometrical measurements of the off gas composition formed in the anodic oxidation or catalytic decomposition of hydrazine at platinized platinum, Raney-nickel and amalgamated sintered nickel as electrocatalysts show that only up to 4% of the oxidation of hydrazine occurs via N—N-bond splitting.

Using ^{15}N marked N_2H_4 we investigated wether the N-N-bond is split in the anodic oxidation or catalytic decomposition of hydrazine. We used platinized platinum (pt. Pt), Raney-nickel (RAN), and amalgamated sintered nickel (SNA) as working electrodes. These materials were chosen, because the reaction mechanism of the anodic oxidation at SNA (direct oxidation of the N_2H_4-molecule in the charge transfer reaction [1]) is different from that at pt. Pt and RAN (preceding dehydrogenation of the N_2H_4 [2]). Therefore, different rates in the splitting reaction were possible at the different electrode materials.

The RAN-electrode consisted of an aluminium-nickel-alloy (1 : 1) which was deposited on a nickel screen by flame-spraying. The sintered-nickel-electrode was amalgamated by loading the porous electrode with hydrogen in 1 m KOH + 1 m $Na(BH_4)$ and afterwards dipping it in to a $HgCl_2$-solution [3]. By this means 1 ml Hg/60 mg Ni was deposited.

Experiments were carried out at the rest-potential (catalytic decomposition) and at a constant overpotential of + 150 mV. Uusually, 2 cm³ off gas at atmospheric pressure were collected and transferred into probe-flask of about 200 cm³, which had been evacuated to 10^{-2} torr and filled several times with argon gas.

All solutions contained 0.2-*m* ^{15}N marked $N_2H_4 \cdot H_2SO_4$ and NaOH at different concentrations:

$0.2\text{-}m\ N_2H_4 \cdot H_2SO_4 + 0.48\text{-}m\ NaOH$,
$0.2\text{-}m\ N_2H_4 \cdot H_2SO_4 + 2.4\text{-}m\ NaOH$ – ,
$0.2\text{-}m\ N_2H_4 \cdot H_2SO_4 + 5.4\text{-}m\ NaOH$.

The relative contents of $H_2{}^{14}N\text{-}{}^{14}NH_2$, $H_2{}^{14}N\text{-}{}^{15}NH_2$, and $H_2{}^{15}N\text{-}{}^{15}NH_2$ in the solution were measured by oxidizing the hydrazine chemically with KJO_3, because in this oxidation reaction no splitting of the N-N-bond occurs [4, 5]. This yielded the following composition for the hydrazine used:

$$H_2{}^{14}N - {}^{14}NH_2 = 96.12\%,$$
$$H_2{}^{14}N - {}^{15}NH_2 = 2.68\%,$$
$$H_2{}^{15}N - {}^{15}NH_2 = 1.20\%.$$

All measurements were carried out at 23, 60, and 90 °C. The results are listed in tables 1 to 6 by giving the $^{29}N_2 : {}^{30}N_2$ ratio. All values are mean-values of 3 – 5 gas probes.

Under the assumption that the N-N-bond is not split, according to the specifications given above, a ratio of $^{29}N_2 : {}^{30}N_2 = 2.68 : 1.20 = 2.24$ should be found. On the other hand, if the N-N-bond is broken, the ratio should be $^{29}N_2 : {}^{30}N_2 = 4.94 : 0.0644 = 76.7$. In this case the produced N-atoms or NH_x-radicals can recombine freely, so that a statistical distribution of the nitrogen-isotopes should be expected. The given ^{14}N- and ^{15}N-portions of 97.46% and 2.54%, respectively, yield

$$^{28}N_2 : {}^{29}N_2 : {}^{30}N_2 = (97.46)^2 : (2 \cdot 97.46 \cdot 2.54) : (2.54)^2$$

or in per cent

$$^{28}N_2 = 94.9\%, \quad ^{29}N_2 = 4.94\%, \quad ^{30}N_2 = 0.0644\%.$$

In all experiments the $^{29}N_2 : {}^{30}N_2$-ratio lies very close to the value of 2.24 expected for the maintenance of the N-N-bond. This value is exactly verified only in a few results with pt. Pt under anodic load. All the other ratios are somewhat larger, so that besides the main reaction a relatively insignificant side reaction with a rupture of the N-N-bond takes place.

The contribution of this side reaction is given in the tables by the per cent rate y, which was calculated with the equation

$$y = \frac{120\,({}^{29}N_2/{}^{30}N_2) - 268}{2.26 + 1.1356\,({}^{29}N_2/{}^{30}N_2)}.$$

This equation can be developed from the system

$$^{29}N_2 = \left(\frac{4.94\,y}{100} + \frac{2.86\,(100-y)}{100}\right)\%,$$
$$^{30}N_2 = \left(\frac{0.0644\,y}{100} + \frac{1.20\,(100-y)}{100}\right)\%.$$

To summarize, one can say that the N-N-bond is maintained to 96 – 98% in the catalytic decomposition of hydrazine. An influence of the OH^--activity, the temperature, or the electrode material was not observed within the limits of error.

In the case of the anodic overpotential of 150 mV, 98 – 100% of the nitrogen obtained is originated

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from a reaction without N-N-rupture. Here, however, an influence of the electrode material was found. The splitting portion of the reaction is particularly small at pt. Pt and significantly greater at RAN. A dependence of OH^--activity or temperature on the splitting reaction was also not found under anodic load.

Finally, it should be mentioned that some experiments have been carried out with lower anodic overpotential and even with cathodic overpotential, and at pt. Pt in acid solutions (1 m H_2SO_4 + 0.05 m $N_2H_4 \cdot H_2SO_4$), too. However, there was no experiment showing more than 4% for the splitting reaction.

Table 1. Solution 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 0.48$ *n* NaOH; rest potential.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.33	2.3	2.31	1.8	2.33	2,3
RAN	2.29	3.6	2.32	2.0	2.32	2.0
SNA	2.38	3.3	2.34	2.5	2.31	1.8

Table 2. Solution: 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 0.48$ *n* NaOH; $\eta = +150$ mV.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.24	0	2.26	0.5	2.27	0.8
RAN	2.29	1.3	2.28	1.0	2.32	2.0
SNA	2.34	2.4	2.25	0.3	2.30	1.5

Table 3. Solution: 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 2.4$ *n* NaOH; rest potential.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.36	2.9	2.38	3.4	2.38	3.4
RAN	2.34	2.4	2.40	3.8	2.39	3.7
SNA	2.33	2.3	2.34	2.5	2.38	3.4

Table 4. Solution: 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 2.4$ *n* NaOH; $\eta = +150$ mV.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.26	0.5	2.25	0.2	2.24	0
RAN	2.30	1.5	2.32	2.0	2.32	2.0
SNA	2.27	0.8	2.29	1.3	2.28	1.0

Table 5. Solution: 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 5.4$ *n* NaOH; rest potential.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.42	4.3	2.33	2.3	2.35	2.6
RAN	2.41	4.0	2.43	4.6	2.36	2.9
SNA	2.38	3.4	2.33	2.3	2.33	2.3

Table 6. Solution: 0.2 *m* $N_2H_4 \cdot H_2SO_4 + 5.4$ *n* NaOH; $\eta = +150$ mV.

Temperature	23 °C		60 °C		90 °C	
Electrode	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]	$^{29}N_2/^{30}N_2$	y [%]
pt.Pt	2.29	1.3	2.26	0.5	2.26	0.5
RAN	2.33	2.3	2.31	1.8	2.33	2.3
SNA	2.26	0.5	2.28	1.0	2.27	0.8

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