Isotopic Studies of the Ammonia Decomposition Reaction Using Lithium Imide Catalyst: Supplementary Information

DATA FITTING PROCEDURES

Mass Spectrometry Data Analysis

Calibration runs of 100% pure Ar, N_2, NH_3 and H_2 were performed in order to ascertain the fragment peak ratios, Table S1. The $^{14}N_2$, $^{15}N_2$ and $^{14}N^{15}N$ species fragmentation patterns were assumed to follow the same probabilities as that of N_2 with natural isotopic abundance. The mass spectrometer collected histograms from m/z = 2 to m/z = 40 (integer steps), which were fitted to linear combinations of the fragmentation patterns in Table S1. A Levenberg-Marquardt least-squares algorithm was used to minimise the error for the fits.[1]

Table S1: Mass Spectrometry Fragmentation Patterns for Pure Gases

Gas (pure)	m/z	Fraction	Associated Fragment
Ar	40	0.8627	$^{40}Ar^{+}$
	36	0.0030	$^{36}Ar^{+}$
	20	0.1343	$^{40}Ar^{++}$
N_2	29	0.0069	$^{14}N^{15}N^{+}$
	28	0.9401	$^{14}N_2^{+}$
	14	0.0530	$^{14}N^{+}$
NH_3	28	0.0149	$^{14}N_2^{+}$
	18	0.0162	$^{14}NH_4^{+}$
	17	0.5209	$^{14}NH_3^{+}$
	16	0.4018	$^{14}NH_2^{+}$
	15	0.0218	$^{14}NH^{+}$
	14	0.0078	$^{14}N^{+}$
	2	0.0166	H_2^{+}
H_2	3	0.0111	H_3^{+}
	2	0.9889	H_2^{+}

Scrambling of N_2 species

The difference between the measured $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ species and their calculated scrambled counterparts are shown to be related as follows. Let the fraction of measured $^{14}N_2$ be a, the measured fraction of $^{14}N^{15}N$ be b and the total N_2 fraction be s (thus, measured $^{15}N_2$ is $t - a - b$). Then:

$$^{14}N_2(\text{measured}) - {}^{14}N_2(\text{calculated}) = a - \left(\frac{a+\frac{1}{2}b}{s}\right)^2 s$$

$$= a - \frac{\left(a+\frac{1}{2}b\right)^2}{s}$$

And:

$$^{15}N_2(\text{measured}) - {}^{15}N_2(\text{calculated}) = s - a - b - \left(1 - \frac{a+\frac{1}{2}b}{s}\right)^2 s$$

$$= s - a - b - \left(s - 2\left(a + \frac{1}{2}b\right) + \frac{\left(a+\frac{1}{2}b\right)^2}{s}\right)$$

$$= a - \frac{\left(a+\frac{1}{2}b\right)^2}{s}$$

Which is the same as the $\Delta^{14}N_2$ expression.
Similarly for $^{14}N^{15}N$:

$$^{14}N^{15}N(\text{measured}) - {}^{14}N^{15}N(\text{calculated}) = b - 2\frac{a+\frac{1}{2}b}{s}\left(1 - \frac{a+\frac{1}{2}b}{s}\right)s$$

$$= b - 2\left(a + \frac{1}{2}b - \frac{\left(a+\frac{1}{2}b\right)^2}{s}\right)$$

$$= -2\left(a - \frac{\left(a+\frac{1}{2}b\right)^2}{s}\right)$$

Which is minus double the $\Delta^{14}N_2$ expression.

Sigmoid fitting

Sigmoid fitting used a Levenberg-Marquardt algorithm to fit to the following function:

$$1 - f_{\mathrm{NH_3}} = 1 - \exp\left(-\exp\left(\frac{A}{R} - \frac{E_A}{RT}\right)\right)$$

where *A* and E_A are fitted parameters, *R* is the gas constant and *T* is the temperature. For the lithium amide only and lithium amide plus iron cases, a more complex function was used, viz:

$$1 - f_{\mathrm{NH_3}} = xC_1 + (1-x)C_2$$

where C_i denoted single Gompertz sigmoid functions (as above) and *x* was a value between 0 and 1.

References

(1) T. J. Wood, J. W. Makepeace, H. M. A. Hunter, M. O. Jones and W. I. F. David, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22999–23006.