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Personal Note

Limericks on nitramide

Dear Editors,

In the past, I have twice published research findings in verse in *Nature*,[1] and have been gratified by the response. The sonnet and haiku used previously have merits as vehicles for scientific communication, but I feel that other verse forms also warrant exploration.

Consequently, I have experimented with limericks in spite of their well-deserved reputation for communicating nonsense.[2] They have an *a*,*a*,*b*,*b*,*a* rhyming sequence with line *a* having three stressed syllables and line *b* having just two; some flexibility is allowed in the number of unstressed syllables in lines *a* and *b*. Their origin is obscure even though they appeared on the English literary scene as late as the mid-nineteenth century, and they usually convey wit rather than philosophical depth. As they have a tradition of being composed spontaneously at times of merriment, I believe they have the potential to communicate the immediate exhilaration that often springs from scientific discovery.

The decomposition of nitramide into nitrous oxide and water is a simple chemical reaction which is known to involve the pre-equilibrium formation of the *aci*-tautomer:

$$\mathrm{NH_2NO_2} \rightleftharpoons \mathrm{HN{=}N(O)OH} \rightarrow \mathrm{N_2O + H_2O}$$

The reaction has been known since the end of the nineteenth century and is of central importance in the development of physical organic chemistry, having been used by Brønsted in the 1920’s to investigate base catalysis.[3]

The Brønsted catalysis law for bases

There once was a chemist called Brønsted
Who did some kinetics and then said:
“The stronger the base,
The faster the pace
Of reaction, as I had expected”.

A comprehensive investigation of the nitramide reaction reported by Kresge provided compelling evidence that the *aci*-tautomer reacts by a stepwise mechanism.[4] He proposed that the conjugate base of the *aci*-tautomer partitions between the rate-determining forward step and its back reaction. We subsequently showed theoretically that this anion is not a viable bonded species, so the base-induced fragmentation of the *aci*-tautomer is necessarily an enforced concerted reaction.[5] The transition structure of this concerted process, however, must be virtually the same as the one in the step-wise alternative in order to satisfy the experimental evidence presented by Kresge. Thus, the proton is very largely transferred in the transition structure, so the concerted reaction is strongly asynchronous,[6] and the mechanism is best seen as a refinement of Kresge’s proposal.

On the concerted nature of the base-induced fragmentation of the *aci*-tautomer of nitramide

The base-induced proton abstraction
Now seems a concerted reaction.
One transition state
Determines the rate,
To everyone’s satisfaction.

The decomposition of nitramide is also catalysed by acids, but this is a much less well known reaction and was rigorously investigated by Cox much later than the base catalysed reaction.[7] We have also been able to show that the protonated form of the *aci*-tautomer of nitramide, proposed by Cox as an intermediate in another step-wise mechanism, is not a bonded species.[5] Consequently, here also, the reaction must be concerted, *i.e.* the putative intermediate has no stability. The elusive nitrous acidium ion ($\mathrm{O{=}N{-}OH_2^+}$) is a simpler analogue of the protonated *aci*-tautomer of nitramide. However, our recent computational investigations indicate that this cation (with the proton on the hydroxy group rather than elsewhere) is a viable species with a pK_a value of about −10 (Ref. 8).

On the possible existence of an intermediate in an acid-induced fragmentation

A molecular fragmentation,
Which is triggered by protonation,
Is concerted or not –
It depends if it's got
Intermediate stabilisation.

The issue of concerted *versus* stepwise fragmentation of chemical species is fundamental to studies of chemical reactivity, and remains a fertile area for collaborative investigations between experimental and computational chemists.[9]

Yours sincerely,

Dr H Maskill

References and footnotes

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3. J. N. Brønsted and K. J. Pedersen, *Z. Phys. Chem.* **108** (1924) 185; a good review of early work on the base-catalysed decomposition of nitramide is given by R. P. Bell in *The Proton in Chemistry*, 2nd ed., Chapman and Hall, 1973.
4. C. H. Arrowsmith, A. Awwal, B. A. Euser, A. J. Kresge, P. P. T. Lau, D. P. Onwood, Y. C. Tang, and E. C. Young, *J. Am. Chem. Soc.* **113** (1991) 172.
5. M. Eckert-Maksić, H. Maskill, and I. Zrinski, *J. Chem. Soc., Perkin Trans.* **2** (2001) 2147.
6. For the distinction between "concerted" and "synchronous", see I. M. Gordon and H. Maskill, *J. Chem. Soc., Chem. Commun.* (1989) 1358.
7. R. A. Cox, *Can. J. Chem.* **74** (1996) 1779.
8. J. Crugeiras, A. Ríos, and H. Maskill, *J. Phys. Chem. A* **115** (2011) 12357.
9. See M. Eckert-Maksić, Z. Glasovac, H. Maskill, and I. Zrinski, *J. Phys. Org. Chem.* **16** (2003) 491, for examples other than proton transfer reactions.