The race for the first generation of the pentazolate anion in solution is far from over†

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The previous claim for the first generation of the pentazolate anion in solution was carefully reexamined; no evidence for the formation of *cyclo*-N_5^- was found under the reported conditions.

The successful synthesis[1] of N_5AsF_6 in 1999 has stimulated worldwide interest in the preparation of new homonuclear polynitrogen species. One of the most promising polynitrogen candidates is the pentazolate anion, *cyclo*-N_5^-. Theoretical calculations[2] predict it to be vibrationally stable, and potential starting materials, *e. g.*, arylpentazoles, have been known for over 50 years.[3] In 2002, the *cyclo*-N_5^- anion was detected in the gas phase, using the *para*-pentazolylphenolate anion as starting material and electrospray negative-ion mass spectrometry as the analytical method.[4] This result was confirmed by laser desorption ionization, time-of-flight mass spectrometry of *N*,*N*-dimethylamino-phenylpentazole.[5] However, attempts to prepare *cyclo*-N_5^- salts in bulk by either the oxidative cleavage of the C–N bond using ozone[6a,b] or the reductive one using alkali metals in liquid ammonia,[6a] were unsuccessful. There is only one claim for the preparation of the *cyclo*-N_5^- anion in solution and its identification by ^{15}N NMR spectroscopy.[7] Using $(NH_4)_2Ce(IV)(NO_3)_6$ (CAN) in aqueous methanol at −40 °C, the *para*-methoxyphenyl group in *para*-methoxyphenylpentazole was oxidized to *para*-benzoquinone, supposedly yielding the zinc salt of the pentazolate anion as coproduct (see Scheme 1).

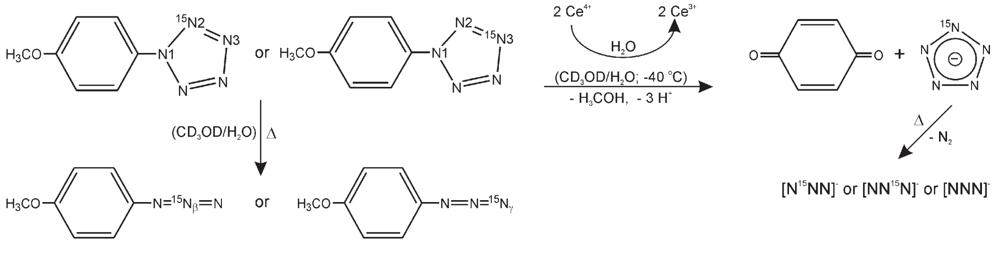
The following ^{15}N NMR evidence was presented[7] for the formation of N_5^-: (i) The observation of a signal at -10 ± 2 ppm which is close to the value predicted[7,8] for N_5^-; and (ii) the observation of two signals at −283 and −147 ppm which were attributed to the terminal and central nitrogen atoms, respectively, of N_3^-, the expected decomposition product of N_5^-.[9] Because the synthesis of the arylpentazole starting material was carried out with azide, singly ^{15}N-labeled only in the terminal position, the appearance of the ^{15}N-label in all positions of the azide decomposition product would be strong evidence for the formation of an intermdiate N_5^- anion in which all nitrogens have become equivalent (see Scheme 1).

Due to the potential of *cyclo*-N_5^- salts as high energy density material (HEDM), we have pursued their bulk synthesis over the past three years. In the course of these studies, we have also reinvestigated the published reaction in more detail.

The $4\text{-}MeOC_6H_4N_5$ starting material was prepared, similar to the method described by Ugi *et al*,[10] by reacting $[4\text{-}MeOC_6H_4N_2][BF_4]$ with NaN_3 in a mixture of MeOH and n-hexane at −40 °C. The only impurities found in the product were small amounts of $[4\text{-}MeOC_6H_4N_2][BF_4]$ and $4\text{-}MeOC_6H_4N_3$. The $4\text{-}MeOC_6H_4N_5$ was suspended in a solution of CAN and $Zn(NO_3)_2$ in CD_3OD/H_2O (77 : 23 v/v) at −78 °C. The concentrations of the salts were the same as previously described.[7] The mixture was warmed to −40 °C and shaken for 2 h at this temperature. We could not obtain a clear solution, and the resulting suspension was centrifuged at −78 °C to compact the solid colorless phase, the Raman spectrum of which at −70 °C showed only signals belonging to the starting material $4\text{-}MeOC_6H_4N_5$ and the NO_3^- anion.

The suspension was warmed from −40 °C to room temperature over a period of 2 days. We could not find any evidence for the formation of *cyclo*-N_5^-, the N_3^- anion or *p*-benzoquinone by Raman and NMR spectroscopy. The only identifiable compound was $4\text{-}MeOC_6H_4N_3$ which originated from the decomposition of $4\text{-}MeOC_6H_4N_5$.

In another experiment the suspension was stirred for 2 h at −40 °C. After the solid had settled, a small amount of dark red mother liquor could be separated and was transferred into an NMR tube at −40 °C. The only species, observable by nitrogen NMR spectroscopy, at −40 and −20 °C were the NO_3^- anion and the NH_4^+ cation.



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details and NMR spectra. See http://www.rsc.org/suppdata/cc/b4/b417010e/

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Most interestingly, the nitrogen signal of the NO_3^- anion was observed in this solvent system at the same chemical shift as the one previously attributed[7] to N_5^-. Furthermore, it was shown that at the given concentrations, this signal was also observable in the ^{15}N NMR spectrum of a solution of CAN/$Zn(NO_3)_2$ in CD_3OD/H_2O without ^{15}N enrichment (the natural abundance of ^{15}N is 0.37%) and in the absence of any other nitrogen containing compounds (Fig. 1).

Therefore, the signal previously observed in the ^{15}N NMR spectrum at −10 ppm and previously attributed[7] to N_5^- is most likely due to the natural abundance signal of the nitrate anion. If the −10 ppm signal were indeed due to N_5^-, two signals should be observed in this region, one for ^{15}N-labeled N_5^- and another one for naturally abundant $^{15}NO_3^-$. In view of the narrow line widths of these signals, an accidental coincidence of their chemical shifts must be considered highly unlikely. The assignment of the −10 ppm signal to NO_3^- is further supported by the surprising persistence of this signal on warm up and the reported[7] changes in relative intensities of the signals on going from −40 to −20 °C. Although no integral values were reported in ref. 7, the peak with the highest intensity in both spectra is the one at $\delta = -10$ ppm. While the intensity of the signals for 4-$MeOC_6H_4N_5$ seem to decrease, the intensities of the signals of the decomposition products increase. This pattern indicates decomposition of 4-$MeOC_6H_4N_5$ rather than that of the compound with a chemical shift at $\delta = -10$ ppm.

The second piece of evidence presented[7] for the formation of N_5^- was the observation of a centrally ^{15}N-labeled N_3^- anion as a decomposition product. A ^{15}N signal at $\delta = -147.2$ ppm was attributed to this nitrogen.

We question this assignment for two reasons. First of all, the previous authors used a 50% excess of CAN, and CAN rapidly oxidizes the azide ion under formation of nitrogen, even at −40 °C.†

$$Ce^{4+} + NaN_3 \xrightarrow[(-40\ ^\circ C)]{(MeOH)} Ce^{3+} + 1\frac{1}{2}\,N_2$$

This is in accord with previous observations, that Ce(IV) salts rapidly oxidize HN_3 in aqueous solution,[11] and was verified by us in control experiments. Actually, CAN can be used for the quantitative analysis of N_3^- in solution.

Secondly, 4-$MeOC_6H_4N_5$ decomposes in MeOH under formation of 4-$MeOC_6H_4N_3$.[3] For 4-$MeOC_6H_4N_5$, which is ^{15}N-labeled at N2 or N3, the resulting decomposition product, 4-$MeOC_6H_4N_3$, is ^{15}N-labeled at either N_β or N_γ (see Scheme 1).

We prepared a sample of 4-$MeOC_6H_4N_3$, ^{15}N-labeled at N_β or N_γ, and recorded its ^{15}N NMR spectrum in CD_3OD. The chemical shift for N_β was found at −135.50 ppm and that for N_γ at −148.16 ppm (Fig. 2).

The chemical shift of −148.16 ppm is very close to that of −147.2 ppm, attributed by the authors of ref. 7 to the central nitrogen of the azide anion. Furthermore, the ^{15}N chemical shifts of the central and terminal nitrogens of NaN_3 in an aqueous solution were observed by us at −133.65 and −281.45 ppm, respectively (Fig. 2). Therefore, the signal at −147.2 ppm should be assigned to N_γ of 4-$MeOC_6H_4N_3$, while that at −283 ppm belongs to the terminal nitrogen of the azide anion. The presence of some azide, which is only terminally labeled, could stem from some unreacted azide starting material. The apparent absence of the −135 ppm signal for N_β of 4-$MeOC_6H_4N_3$ in Fig. 3 of ref. 7 might be due to the relatively poor signal to noise ratio in their spectrum and the fact that the peak height of N_β is considerably lower than that of N_γ (see Fig. 2).

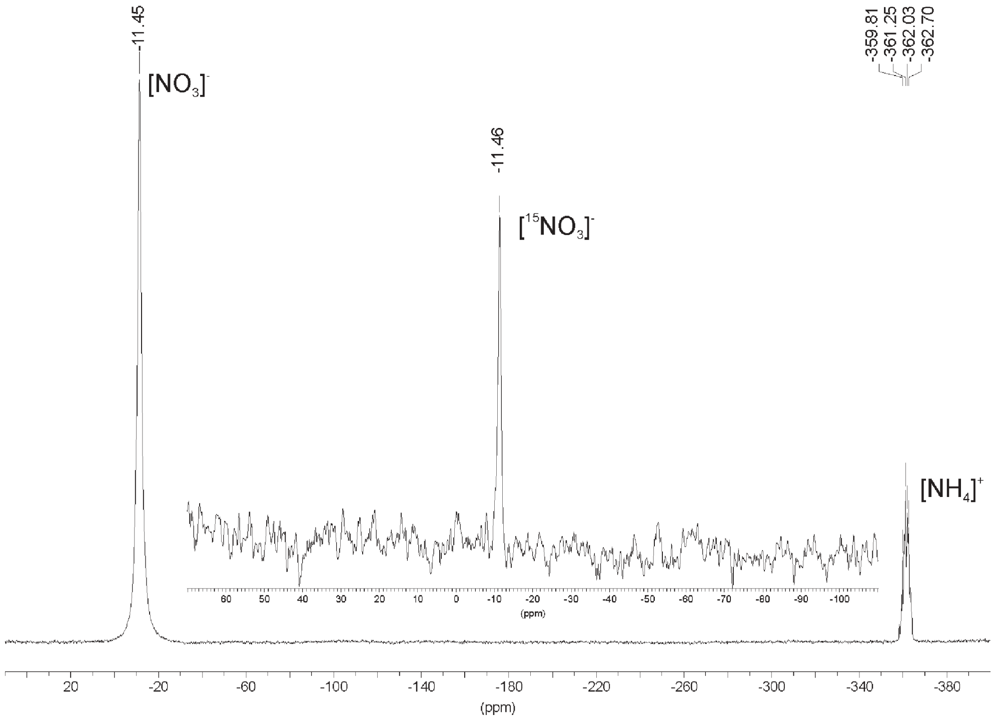

Fig. 1 ^{14}N NMR (inset ^{15}N NMR) spectrum of CAN/$Zn(NO_3)_2$ (1 : 2.1) in CD_3OD/H_2O at rt.; δ (external CD_3NO_2) = 0 ppm.

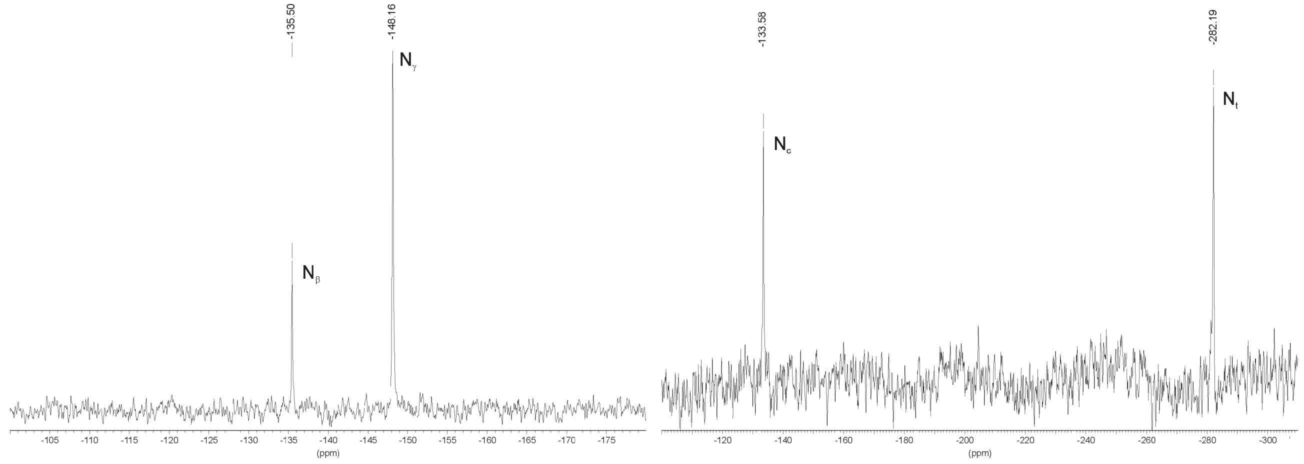

Fig. 2 ^{15}N NMR spectrum of 4-MeOC$_6$H$_4$N$_3$ in MeOH (left) and ^{15}N NMR (natural abundance) spectrum of NaN$_3$ in H$_2$O (right). δ (external CD$_3$NO$_2$) = 0 ppm.

In summary, we conclude that the previous claim[7] for the first observation of the pentazolate anion in the condensed phase is insufficiently supported. In our opinion the peak in the previously published[7] spectra at -10 ± 2 ppm is due to the nitrate anion, while the peak at -147.2 ppm belongs to N$_\gamma$ of the decomposition product 4-MeOC$_6$H$_4$N$_3$. Neither the pentazolate anion nor the important decomposition product, the azide anion, ^{15}N-labeled at the central nitrogen atom, have been observed. Therefore, the race for the first successful synthesis and observation of *cyclo*-N$_5^-$ in the condensed phase is still open.

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