

^{15}N CIDNP IN AZO COMPOUND DECOMPOSITION

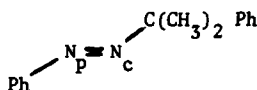
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^{15}N CIDNP has been used as a mechanistic tool in studies related to diazo coupling¹ and triazene decomposition.² Lipmaa, in particular,² has pointed out the sensitivity of the ^{15}N nucleus as a mechanistic probe in CIDNP studies. We report here an ^{15}N CIDNP study of the unsymmetric azo compound **1**. The interpretation of the ^{15}N CIDNP spectra reported here is particularly straightforward and provides support for the intermediacy of diazenyl radicals ($\text{R-N=N}\cdot$) during decomposition of unsymmetric azo compounds.

trans-1 can be readily obtained labelled with either 97% ^{15}N at the nitrogen attached to the phenyl group (N_p) or 50% ^{15}N at the nitrogen attached to the cumyl group (N_c).³ **trans-1** was photoequilibrated at -80° and **cis-1** was isolated as previously reported.⁴ ^{15}N spectra were obtained on a Bruker HFX 10 pulse spectrometer. Chemical shifts⁵ in ppm downfield from $^{15}\text{NO}_3^-$ were **trans-1**; $\text{N}_p = 132$, $\text{N}_c = 170$; **cis-1**, $\text{N}_p = 161$, $\text{N}_c = 194$.



trans-1

In the figure is presented the undecoupled ^{15}N CIDNP spectrum obtained during decomposition (benzene solvent) of **cis-1** labelled at either N_p or N_c . For the N_p labelled compound (part a) strong enhanced absorption (A) is observed for N_p of **cis-1** and **trans-1**. In

addition, a strong emission (E) is observed 66.5 ppm upfield from NO_3^- . The ^{15}N CIDNP spectrum for the N_c labelled azo compound is presented in Fig 1 (b). Enhanced absorption is observed for signals due to N_c in cis- λ and trans- λ . In addition, emission 66.5 ppm upfield from $^{15}\text{NO}_3^-$ is also observed.

The ^{15}N CIDNP spectrum from cis- λ is easier to detect than corresponding ^1H or ^{13}C spectra.⁶ ^1H and ^{13}C spectra from cis- λ must be obtained near 40° where decomposition is fast.⁴ Easily detectable ^{15}N CIDNP spectra can be obtained at temperatures below 20° where the half life of cis- λ is greater than 30 min.. ^{15}N would thus appear to be the nucleus of choice in terms of sensitivity, for CIDNP studies in azo decompositions.

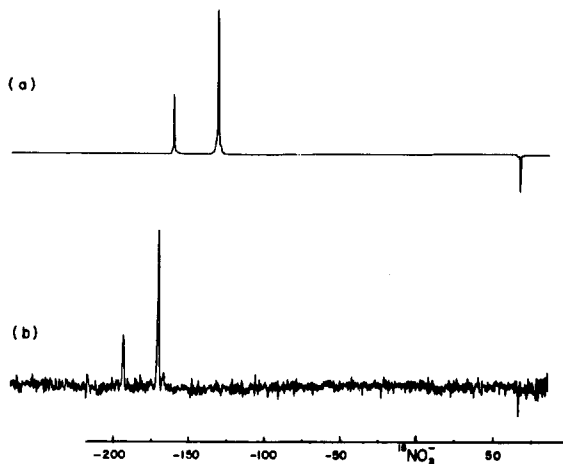
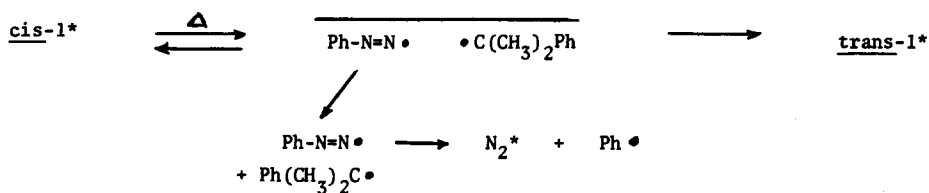


Figure. ^{15}N CIDNP from (a) N_p and (b) N_c labelled cis- λ

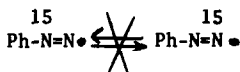
The ^{15}N CIDNP spectra obtained from cis- λ decomposition are consistent with the mechanism outlined in the Scheme, where * indicates products which are polarized. On the basis of this Scheme, several mechanistic conclusions can be drawn.



SCHEME

(1) Since N_p and N_c labelled cis-l both give rise to enhanced absorption CIDNP signals in cis and trans-l, application of the CKO rules⁷ suggests that the hyperfine coupling constants of N_p and N_c in the phenyldiazanyl radical must both be positive.⁸

(2) Since N_p labelled cis-l only gives rise to N_p CIDNP signals, no significant scrambling of N_p and N_c occurs in Ph-N_2 .⁹ Rearrangement similar to that observed in



phenyldiazonium salt¹⁰ decompositions is apparently not competitive with other pathways available to the radical.

(3) The E signal observed 66.5 ppm \pm 1.0 ppm upfield from $^{15}\text{NO}_3^-$ must be due to molecular nitrogen, $^{29}\text{N}_2$, formed by β -scission of escape phenyldiazanyl radicals. The fact that both N_p and N_c labelled compounds give rise to this emission signal requires that the species responsible be an escape product that is symmetric with respect to N_p and N_c . The chemical shift of N_2 has been the subject of some controversy. N_2 signals 14 and 70 ppm upfield from NO_3^- have been reported.^{11,12} The latter claim has recently been supported by Roberts *et. al.*¹³ who report a chemical shift for liquid $^{29}\text{N}_2$ 67.6 \pm 1.5 ppm upfield from $^{15}\text{NO}_3^-$. Our value for the chemical shift of $^{29}\text{N}_2$ at 35° is thus consistent with values reported earlier for liquid N_2 .

We should point out that examination of the published ^{15}N CIDNP spectra of other workers reveals signals which may be due to polarized $^{29}\text{N}_2$. In particular, published ^{15}N CIDNP spectra by Bubnov *et. al.*¹ show emission at about 65 ppm¹⁴ which most likely is due to $^{29}\text{N}_2$. Application of the CKO rules suggests that $^{29}\text{N}_2$ should be observed in emission in this system. Finally, we note that Lipmaa² also observes an emission at 65 ppm in his studies of triazenes. Although he does not assign this emission to $^{29}\text{N}_2$, the CKO rules suggest here also that, if formed from triazenes, $^{29}\text{N}_2$ would be observed in emission.

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5. Chemical shifts are referred to 5.8 M $^{15}\text{NH}_4^{15}\text{NO}_3$ in 2 M HNO_3 .
6. ^{13}C CIDNP of cis-1 will be presented elsewhere.
7. The following parameters were assumed: $g(\text{PhN}_2\cdot) < g(\text{Ph}(\text{CH}_3)_2\text{C}\cdot)$. Sign of hyperfine C_p in $\text{PhN}_2\cdot$ + ; C_c in $\text{Ph}(\text{CH}_3)_2\text{C}\cdot$ + ; C_β in $\text{Ph}(\text{CH}_3)_2\text{C}\cdot$ - . N_p and N_c in $\text{Ph-N}_2\cdot$, + [See ref. 8 and J. Pople, D. Beveridge, P. Dodosh, J. Amer. Chem. Soc., **90**, 4201(1968)].
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14. N_2 would be the escape product from a phenyldiazenyl-phenoxy radical pair.