

E.S.R. Detection of Alkylideneamino Radicals in the Reaction of Nitrogen Atoms with Alkenes

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Summary Intermediates formed in the gas-phase reaction of nitrogen atoms with alkenes have been trapped in an inert matrix using a rotating cryostat, e s r examination of the frozen samples has shown the presence of methyleneamino ($\text{CH}_2=\text{N}\cdot$) and alkylideneamino ($\text{RCH}=\text{N}\cdot$) radicals

DESPITE the extensive studies of the reactions of ground state nitrogen atoms¹ with alkenes there is still considerable uncertainty about the detailed mechanism whereby the hydrocarbon is converted almost exclusively into hydrogen cyanide². This uncertainty arises in part from the failure to detect any of the nitrogen-containing intermediates in these systems although both reactants and stable product

molecules have been monitored continuously by mass spectrometric microprobe methods. Here we present a preliminary report of the e s r detection of such intermediates by the use of similar microprobe sampling techniques in conjunction with a rotating cryostat.

Nitrogen atoms ($ca\ 4\ \text{N m}^{-2}$) produced in a stream of purified molecular nitrogen ($ca\ 400\ \text{N m}^{-2}$) in a 28 MHz radio-frequency discharge were mixed with the alkene ($ca\ 40\ \text{N m}^{-2}$) in a silica tubular reactor (1.5 cm i d) which had a small sampling orifice ($ca\ 0.05\ \text{cm}$) through which stable molecules and metastable intermediates, after a residence time of $ca\ 10^{-3}\ \text{s}$, could be leaked to be trapped in an inert matrix on the drum of a rotating cryostat. In this technique³ a drum containing liquid nitrogen rotates at

high speed (ca. 2400 r.p.m.) in a vacuum chamber. A jet located a few millimetres from the drum allows the vapour of the inert matrix to be rapidly condensed to form a fresh solid layer a few monolayers thick per revolution of the drum. The exit of the sampling orifice is also placed close to the drum surface so that the reaction mixture sample continuously condenses on the renewed moving surface of the inert matrix. Reactive intermediates are trapped on the surface of the solid and covered with the next layer of condensed inert vapour which itself is covered with a new layer of reactive intermediates. This process is repeated for each revolution and at the end of an experiment (30 min) the interleaved spiral deposit (ca. 2–3 mm thick) can be transferred at 77 K and under vacuum to tubes suitable for e.s.r. examination of free radical intermediates trapped out of the gas phase reactor.

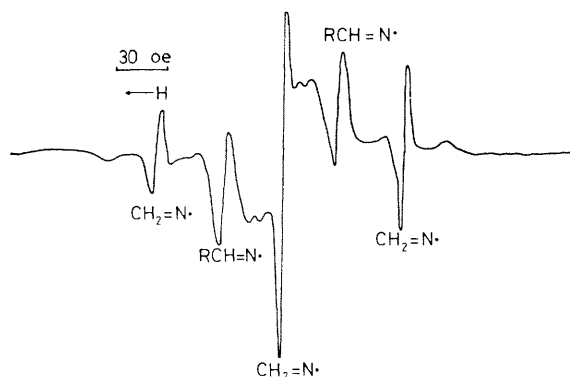
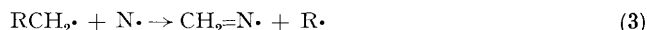
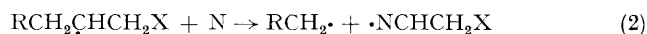
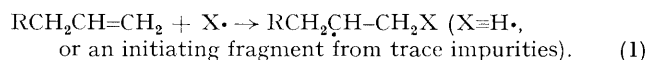


FIGURE. First derivative e.s.r. spectrum at 77 K of a sample trapped from the reaction of nitrogen atoms with *trans*-2,6-dimethylhex-3-ene in the gas phase at 298 K.

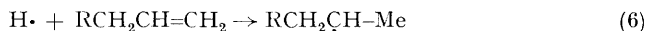
The e.s.r. spectrum of the deposit from the reaction of nitrogen atoms with *trans*-2,6-dimethylhex-3-ene at 25 °C using water as the trapping matrix is shown in the Figure. The spectrum can be unambiguously assigned to two radicals, the methyleneamino radical, $\text{CH}_2=\text{N}\cdot$ and an alkylidene-amino radical, $\text{RCH}=\text{N}\cdot$. No other radicals are present in significant amounts. The triplet of triplets is very similar to that observed previously for $\text{CH}_2=\text{N}\cdot$ in the solid phase⁴ and has the highly characteristic large isotropic hydrogen hyperfine interaction of 81 Oe and a much smaller anisotropic nitrogen interaction of 10 Oe. The doublet of triplets again has the characteristically high hydrogen interaction observed for radicals such as $\text{MeCH}=\text{N}\cdot$.⁵ Similar spectra indicating the presence of similar concentrations of only $\text{CH}_2=\text{N}\cdot$ and $\text{RCH}=\text{N}\cdot$ radicals are observed for the reactions of nitrogen atoms with pent-1-ene and *cis*

and *trans*-hex-2-ene. When nitrogen atoms were allowed to react with *trans*-2,2',6,6'-tetramethylhex-3-ene and di-*t*-butylethylene the spectrum showed that, in addition to $\text{CH}_2=\text{N}\cdot$ and $\text{RCH}=\text{N}\cdot$ there were appreciable amounts of *t*-butyl radicals and an alkyl radical derived from the parent alkene without fragmentation. In the case of ethylene, propene, methylpropene, and buta-1,3-diene no amino radicals were detected but appreciable amounts of ethyl-, isopropyl-, *t* butyl-, and methyl-substituted alkyl radicals, respectively, were observed. It is significant that in no case was there any evidence for the occurrence of triplet nitrene radicals although a thorough search for these species was made.

Our results provide the first direct evidence for the correctness of Saffrany's suggestion that $\text{CH}_2=\text{N}\cdot$ radicals are important intermediates in nitrogen atom alkene reactions⁶ and also show the equal importance of alkylidene-amino radicals. The results reported here, together with our finding of no reaction whatsoever occurring on the bombardment of alkenes at 77 K with nitrogen atoms⁷ suggest that the following reactions are amongst the most important in nitrogen atom alkene systems. Most of the nitrogen atoms are removed not by direct reaction with the alkene but by reaction with alkyl radicals, in agreement with results from studies at low nitrogen atom levels.⁸



(Further reactions of $\text{R}\cdot$ and fragments to produce $\text{R}'\text{CHN}\cdot$ and $\text{CH}_2\text{N}\cdot$)



The alkyl radical–nitrogen atom reactions are cracking reactions which may proceed through nitrene radicals $\text{RN}\cdot$. In this case they are analogous to the well known β scission reactions of the closely related alkoxy radicals. It is interesting that in the short reaction times used in our system no nitrogen intermediates are found in the case of ethylene, propene, methylpropene, and buta-1,3-diene. If the nitrene radicals were formed in these cases the amino radicals could be formed only by carbon–methyl or carbon–vinyl cleavage. The corresponding β scission reactions are also much slower⁹ in alkoxy radicals.

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