An Electron Spin Resonance Study of the Photolysis of Azide Ions in Liquid Ammonia: Formation of Imine Radical Anions in the Presence of Alkenes

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U.v. photolysis of ammonia or ammonia-ethereal solutions containing sodium or tetra-n-butylammonium azide leads to the formation of the diazene radical anion $[HN{=}NH]^{-\bullet}$, which is detectable by e.s.r. spectroscopy. The e.s.r. spectrum of the ammonia-solvated electron is also observed and the primary photochemical process is probably ejection of an electron from N_3^- to give the azido radical $N_3^\bullet$. Addition of $N_3^\bullet$ to ammonia and subsequent loss of nitrogen accompanied or followed by a hydrogen shift would give the hydrazyl radical, deprotonation of which gives $[HN{=}NH]^{-\bullet}$. In the presence of mono- or 1,1-di-alkylated ethenes, $R^1R^2C{=}CH_2$, the spectrum of $[HN{=}NH]^{-\bullet}$ is replaced by one assigned to the imine radical anion $[R^1R^2CH{-}C(H){=}NH]^{-\bullet}$; possible routes for formation of such species following addition of $N_3^\bullet$ to the alkene are discussed.

In suitable solvents, anions with relatively low ionisation potentials exhibit optical absorption in the near u.v. region which results from electron transfer to the solvent.[1,2] For a given anion, the wavelength of the charge-transfer-to-solvent (c.t.t.s.)[1] band depends on the temperature and, more markedly, on the nature of the solvent. The c.t.t.s. energies are comparatively small in ammonia, but are larger in hydroxylic media (*e.g.* $\lambda_{max.}$ for I^- is 264 nm in NH_3 and 226 nm in H_2O at 293 K; $\varepsilon_{max.}$ *ca.* 1×10^4 l mol^{-1} cm^{-1} in both solvents).

A number of e.s.r. studies have confirmed the occurrence of electron photo-detachment from anions, for example during photolysis of alkali metal amides in liquid amines.[3,4] We have recently reported that overlapping e.s.r. spectra of the borane radical anion and of the solvated electron may be detected during continuous u.v. photolysis of tetra-n-butylammonium borohydride in ammonia–1,2-dimethoxyethane (DME) [equation (1)].[5]

$$H_4B^- \xrightarrow[-e^-_{amm.}]{h\nu} [H_4B^\bullet] \xrightarrow[-NH_4^+]{NH_3} H_3B^{-\bullet} \qquad (1)$$

Aqueous solutions containing the azide ion (N_3^-) exhibit two strong overlapping optical absorption bands above 200 nm.[2,6] The band at 203 nm ($\varepsilon_{max.}$ *ca.* 4×10^3 l mol^{-1} cm^{-1}) has been assigned as a c.t.t.s. transition; the weaker band at 230 nm ($\varepsilon_{max.}$ 4×10^2 l mol^{-1} cm^{-1}) is thought to originate from an intramolecular electronic transition ($^1\Delta_u \longleftarrow {}^1\Sigma_g{}^+$).[6] In ammonia solvent the c.t.t.s. band should be red-shifted by *ca.* 40 nm, whilst the energy of the intramolecular transition is likely to be relatively little changed.[2]

In this paper we report an e.s.r. study of the radicals produced during u.v. photolysis of tetra-n-butylammonium or sodium azide in liquid ammonia in the presence and absence of simple alkenes.

Results

E.s.r. spectra were recorded during continuous irradiation of samples in the cavity of the spectrometer.[7] The light source was a 500 W high-pressure mercury arc (Osram HBO 500 W/2) and the beam was passed through an aqueous filter solution containing nickel and cobalt sulphates, which removes most of the i.r. and some of the visible radiation.[8] The majority of the u.v. light incident on the sample is in the wavelength region 240—340 nm. Optical absorption by the azide ion 'tails' into this region in both water–DME and ammonia–DME solvent systems, but the absorption is stronger in the latter mixture, as expected for a c.t.t.s. transition. At room temperature in 2 mm path-length quartz cells, solutions of sodium azide (2.3×10^{-2}M) in NH_3–DME (2:1 v/v) and in H_2O–DME (2:1 v/v) absorbed >99% and only *ca.* 50%, respectively, of the incident light at 260 nm. Thus, we can be fairly confident that in our experiments most of the u.v. radiation is inducing the c.t.t.s. transition of N_3^-, although formation of an intramolecular electronically excited state probably also takes place to a small extent.

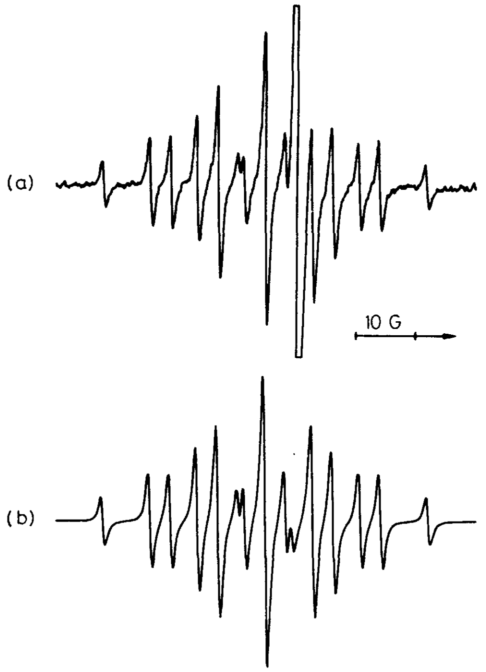


Figure 1. (a) E.s.r. spectrum obtained during photolysis of sodium azide in liquid ammonia at 227 K; the strong line towards the centre is due to $e^-_{amm.}$. (b) Computer simulation of the spectrum of the diazene radical anion (1) based on the parameters given in the text

The e.s.r. spectrum shown in Figure 1 was recorded during photolysis of a solution of sodium azide (*ca.* 0.06M) in liquid ammonia at 227 K. A similar spectrum was obtained from a saturated solution of NaN_3 in NH_3–dimethyl ether (2:1 v/v) or when tetra-n-butylammonium azide (TBAA; *ca.* 0.2M) replaced the sodium salt in this solvent or in NH_3–DME (2:1 v/v). The

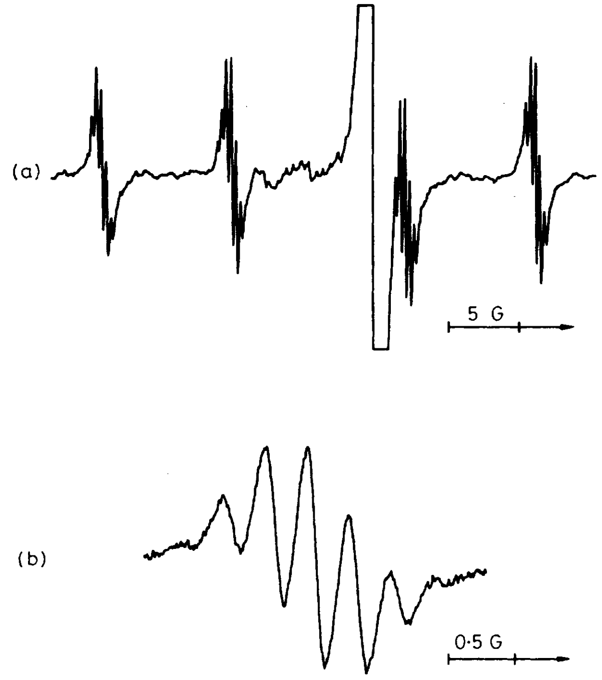


Figure 2. (a) E.s.r. spectra of the imine radical anion (**2**) and the solvated electron obtained during photolysis of an NH_3–Me_2O (2:1 v/v) solution containing TBAA and 2-methylpropene at 219 K. (b) Expansion of the lowest-field multiplet in the e.s.r. spectrum of (**2**) at 240 K

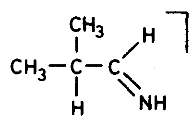
intense single line at *g* 2.0011 is assigned to the ammonia-solvated electron[9,*] and the remaining lines arise from a radical in which the unpaired electron is coupled to two equivalent protons and two equivalent nitrogen nuclei [*a*(2H) 11.3, *a*(2N) 7.9 G, *g* 2.0043 at 227 K]. On the basis of these spectroscopic parameters we propose that the species responsible for the multiline spectrum is the diazene radical anion $[HN{=}NH]^{-\cdot}$ (**1**), which is the conjugate base of the hydrazyl radical $H_2N\dot{N}H$ [*a*(1H) 16.3, *a*(1H) 4.3, *a*(1H) 1.6, *a*(1N) 11.7, *a*(1N) 8.8 G, *g* 2.0037 at 273 K in benzene].[10] Strong support for this assignment was provided by the observation of the same spectrum, along with that of $e^-_{amm.}$, during photolysis of a solution containing hydrazine and potassium t-butoxide (both *ca.* 0.4M) in NH_3–tetrahydrofuran (THF) (1:1 v/v). The hydrazide anion would be expected to exhibit low-energy c.t.t.s. absorption in ammonia solutions[1,2] and we propose that (**1**) is formed as shown in equations (2) and (3). When photolysis of sodium azide in ammonia was interrupted, decay of the e.s.r. spectrum of (**1**) followed approximately first-order kinetics with a half-life of *ca.* 0.5 s at 227 K.

$$\mathrm{Bu^tO^- + H_2NNH_2 \rightleftharpoons Bu^tOH + H_2N\bar{N}H} \qquad (2)$$

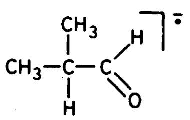
$$\mathrm{H_2N\bar{N}H \xrightarrow[-e^-_{amm.}]{h\nu} H_2N\dot{N}H \xrightarrow{-H^+} \underset{(\mathbf{1})}{[HN{=}NH]^{-\cdot}}} \qquad (3)$$

Photolysis of Azide Ions in the Presence of Alkenes.—In order to maintain sample homogeneity, it was necessary to carry out these experiments with TBAA (0.1—0.3M), since with sodium or lithium azides liquid-phase separation could not be avoided.

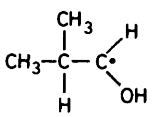
Photolysis of a solution containing TBAA (0.2M) and 2-methylpropene (*ca.* 2M) in NH_3–Me_2O (2:1 v/v) gave rise to a



(**2**)



(**3**)



(**4**)

strong e.s.r. spectrum consisting of four equally intense binomial septets, along with the signal from $e^-_{amm.}$ (see Figure 2).† The spectrum of (**1**) was barely detectable and very much weaker than in the absence of alkene. The four groups of lines result from coupling to two non-equivalent protons and the additional septet splitting presumably arises from two equivalent methyl groups. The e.s.r. parameters [$a(1H_\beta)$ 21.5, $a(1H_\alpha)$ 9.3, $a(6H_\gamma)$ 0.3 G, g 2.0039 at 213 K] and the further considerations detailed below lead us to assign this spectrum to the imine radical anion (**2**).‡ Similar results were obtained in the absence of an ether co-solvent, although much of the alkene was now present in a second liquid phase. Surprisingly, no nitrogen hyperfine splitting was detected for (**2**), nor for any of the other imine radical anions (IRAs) generated in this work, and therefore experiments were carried out to confirm that the 2-methylpropanal radical anion (**3**), which conceivably might be formed by adventitious oxidation processes, was not responsible for the spectrum attributed to (**2**).

An e.s.r. spectrum which we assign to (**3**) {$a(1H_\beta)$ 21.3, $a(1H_\alpha)$ 12.0 G, *g* 2.0035 at 220 K, $d[a(H_\beta)]/dT$ −24 mG K^{-1}} was observed during photolysis of a solution containing sodium 2-methylpropylate (*ca.* 0.1M) in NH_3–2-methylpropan-1-ol (2:1 v/v); the solvated electron (*g* 2.0014) was also detected. When the sodium alkoxide was replaced by di-t-butyl peroxide (NH_3–Bu^tOH–Bu^tOOBu^t 4:2:1 v/v), the spectrum of the α-hydroxyalkyl radical (**4**) [of which (**3**) is the conjugate base] was detected and coupling from the hydroxy proton was clearly resolved in this less basic system {$a(1H_\beta)$ 22.8, $a(1H_\alpha)$ 13.7, *a*(O*H*) 1.1 G, *g* 2.0033 at 238 K, $d[a(H_\beta)]/dT$ −22 mG K^{-1} between 218 and 287 K}. Formation of (**3**) probably involves c.t.t.s. from H_2N^- or RO^- to give a neutral radical capable of abstracting hydrogen from the alkoxide ion (or the alcohol), whilst (**4**) is produced following light absorption by the peroxide [equations (4) and (5)] in a medium insufficiently basic to bring about deprotonation of the hydroxyalkyl radical.

$$\mathrm{Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\cdot} \qquad (4)$$

$$\mathrm{Bu^tO^\cdot + (CH_3)_2CHCH_2OH \longrightarrow (CH_3)_2CH\dot{C}HOH + Bu^tOH} \qquad (5)$$

To help define the route by which the IRAs are formed, experiments were carried out with perdeuterio-2-methylpropene. Photolysis of TBAA in the presence of this alkene gave rise to the spectra of two IRAs identified as (**5**) and (**6**) (the lines marked D and H, respectively, in Figure 3). The relative intensity of the spectrum of (**6**) increased as photolysis proceeded [compare Figures 3(a) and (b)], but extrapolation back to zero irradiation time indicated that only (**5**) was present initially. A limiting value for [(**5**)]/[(**6**)] of *ca.* 1.7 was reached after 30 min irradiation at 223 K. Evidently the α-deuterium in a

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[*] The *g*-factor of $e^-_{amm.}$ was 2.0011 in ammonia and 2.0013 in NH_3–Me_2O or NH_3–DME (2:1 v/v).

[†] It was usually necessary to irradiate samples for a few minutes before e.s.r. spectra were detected. We attribute this induction period to the presence of traces of water which must be consumed before the concentration of radical anions or solvated electrons can build up to detectable levels.

[‡] When the light was shuttered at 213 K, decay of the spectrum of (**2**) followed mixed first- and second-order kinetics with a half-life of *ca.* 5 s.

Table. E.s.r. parameters for imine radical anions $[R^1R^2C(H_\beta){-}C(H_\alpha){=}NH]^{-\bullet}$ (7) in NH_3-Me_2O (2:1 v/v)

R^1	R^2	T/K	g-Factor	Hyperfine splittings (G) $a(1H_\alpha)$	$a(H_\beta)$[a]	$a(H_\gamma)$[a]
Me	Me	213	2.0039	9.3	21.5(1)	0.3(6)
		255		9.0	20.5(1)	0.3(6)
CD_3[b]	CD_3[b]	212	2.0038	1.4[c]	21.6(1)	
		250	2.0038	1.4[c]	20.8(1)	
Et	Et	212		10.2	18.4(1)	*d*
		240	2.0038	10.0	18.0(1)	*d*
$-CH_2CH_2CH_2CH_2CH_2-$		233		9.2	18.6(1)	*ca.* 0.6(4)
Me	Pr^i	228		10.1	20.3(1)	*d*
Me[e]	Bu^t[e]	214	2.0038	10.5	16.1(1)	*d*
		250	2.0038	10.2	15.6(1)	*d*
Me	Bu^tCH_2	233	2.0038	8.9	22.8(1)	*ca.* 0.7(1)
Me	H	205	2.0038	9.8	20.4(1)	0.6(3)
Et	H	223	2.0039	10.0	18.8(2)	*ca.* 0.7(2)
Bu^t	H	205	2.0039	10.9	15.9(3)	
		235	2.0039	10.9	15.3(2)	

[a] Number of equivalent protons in parentheses. [b] Imine radical anion (**5**). [c] Deuterium splitting. [d] Not resolved. [e] At 225 K decay of the IRA followed approximately first-order kinetics when the light was shuttered; the half-life was *ca.* 1.5 s. The spectrum of $e^-_{amm.}$ decayed within the fall-time of the spectrometer (0.2 s).

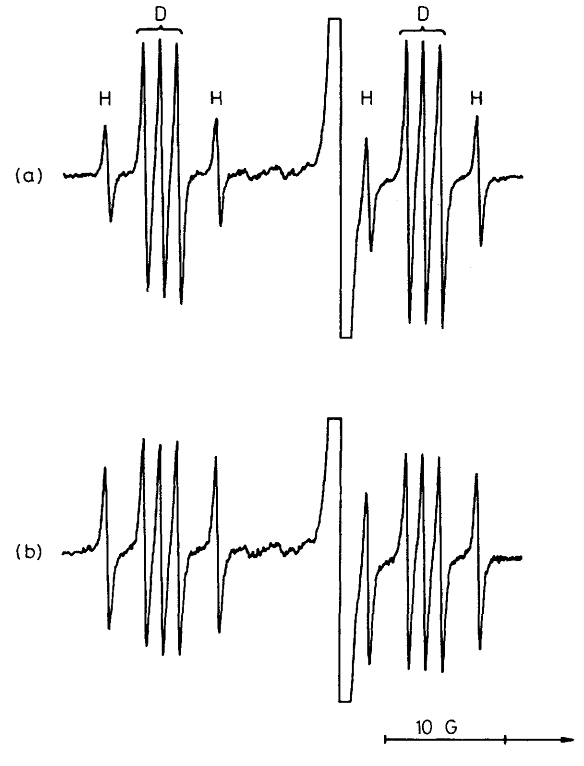
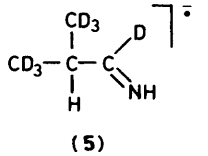
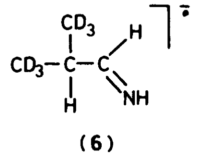


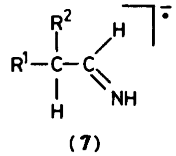
Figure 3. E.s.r. spectra of the imine radical anions (**5**) and (**6**) (lines marked D and H, respectively) along with $e^-_{amm.}$ recorded during photolysis of an NH_3-Me_2O (2:1 v/v) solution containing TBAA and perdeuterio-2-methylpropene at 223 K: (b) was recorded a few minutes after (a)



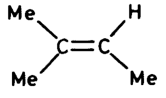
(**5**)



(**6**)



(**7**)



(**8**)

precursor of the IRA is exchangeable with the solvent NH_3. No IRA with deuterium attached to the β-carbon atom was detected, confirming that the β-proton originates from the solvent.

A number of other IRAs were generated by photolysis of azide ions in the presence of a variety of terminal alkenes $R^1R^2C{=}CH_2$ (R^1 = alkyl, R^2 = H or alkyl) and the e.s.r. parameters (see Table) are fully in accord with the structure (**7**). With the monosubstituted ethenes a relatively strong spectrum of $[HN{=}NH]^{-\bullet}$ was detected alongside that of (**7**), while with the 1,1-disubstituted ethenes the spectrum of the diazene radical anion was very much weaker (see Figures 2 and 3). With ethene itself, no spectrum attributable to (**7**; $R^1 = R^2 = H$) was observed and only $[HN{=}NH]^{-\bullet}$ and $e^-_{amm.}$ were detected.

To our surprise 2-methylbut-2-ene (**8**) afforded an IRA spectrum identical with that assigned to (**2**) and obtained from 2-methylpropene. However, in addition to the spectrum of $e^-_{amm.}$ some unidentified signals were also present and the spectrum of (**2**) took longer to develop than when it was derived from 2-methylpropene. The sample of (**8**) was shown by g.l.c. analysis to contain <0.1% 2-methylpropene.

2,3-Dimethylbut-2-ene (tetramethylethene) gave no spectrum attributable to an IRA, even after prolonged irradiation. The spectrum of $e^-_{amm.}$ was present, but that of (**1**) was not detectable.

In order to explore the possibility that aziridines might be intermediates in the formation of the IRAs, an NH_3-Me_2O solution containing TBAA and 2-methylaziridine (*ca.* 0.5M) was irradiated. However, only (**1**) and $e^-_{amm.}$ were detected and no spectrum of (**7**; R^1 = Me, R^2 = H) was observed.

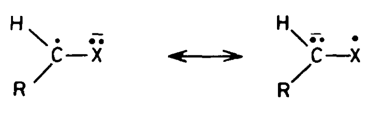
When (**1**) was generated from hydrazine and potassium t-butoxide (see before) in the presence of 2-methylpropene (*ca.* 1M) again only (**1**) and $e^-_{amm.}$ were detected, showing that the diazene radical anion does not react with the alkene under these conditions to produce an IRA.

Discussion

The intense optical absorption in the near u.v. region exhibited by N_3^- in liquid ammonia or mixed ether–NH_3 solvents undoubtedly originates mainly from a c.t.t.s. transition.[1,2,6] However, there is probably also some contribution to this absorption from an intramolecular electronic transition[2,6] of N_3^- and thus, although we consider it unlikely, we cannot eliminate the possibility that a reaction of electronically excited N_3^- could be involved in the formation of the diazene and imine radical anions detected by e.s.r. spectroscopy.

The diazene radical must be non-linear[11] and probably has a near-planar *trans*-structure in which the unpaired electron occupies a π^* N–N molecular orbital.

The unpaired electron in an IRA is expected to reside in a π^* C–N orbital and the electronic configuration may be represented as a hybrid of structures (**8a** and **b**; X = NH), with the former making the larger contribution because nitrogen is more electronegative than carbon. The isoelectronic aldehyde radical anions[12,13] (**8**; X = O) and the more common ketyls[14] may be similarly represented and, since oxygen is more electronegative than nitrogen, the relative contribution of (**8a**) will be greater than for the IRAs. In both imine and aldehyde radical anions the arrangement of bonds about the C–X group probably does not deviate very much from planarity.[12]



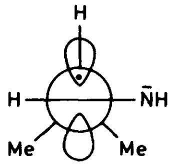
(**8a**) (**8b**)

It is surprising that no ^{14}N hyperfine splitting is resolvable in the e.s.r. spectra of the IRAs [$a(N) \leqslant 0.15$ G for (**2**); see Figure 2], although it is resonable that this splitting should be small since there will be two contributions of opposite sign to $a(N)$. π-Spin population on nitrogen will give rise to a positive contribution to $a(N)$, whilst π-spin population on carbon [see (**8a**)] will result in a negative contribution to $a(N)$ arising from polarisation of the C–N σ bonding electrons.

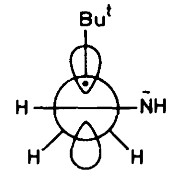
It is also conceivable that exchange of nitrogen in an IRA with that in the ammonia solvent could take place readily by an addition–elimination mechanism, and no nitrogen hyperfine splitting would be detectable if exchange occurs rapidly on the e.s.r. timescale. Similarly, rapid exchange with protons in the ammonia solvent is presumably responsible for the absence of detectable splitting from the imino proton in an IRA.

The magnitudes of the α- and β-proton splittings for the IRAs are reasonable in comparison with those shown by (**3**) and by the acetaldehyde radical anion[12,13] $[CH_3C(H)=O]^{-\cdot}$ [$a(1H_\alpha)$ 11.1, $a(3H_\beta)$ 20.2 G, g 2.0036 in water at room temperature]. It is noteworthy that the g-factors of the IRAs are somewhat greater than those of the aldehyde radical anions and the ketyls, despite the larger spin–orbit coupling of oxygen as compared with that of nitrogen, reflecting the shift of spin from the heteroatom to carbon on going from (**8**; X = NH) to (**8**; X = O). This shift of spin density is also reflected in the magnitudes of $a(H_\alpha)$ shown by (**2**) and (**3**).

Substituent effects on the magnitudes of the β-proton splittings shown by the IRAs may be interpreted in terms of conformational effects and the well known torsion angle dependence of $a(H_\beta)$.[15] The magnitude of $a(1H_\beta)$ for (**2**) and its negative temperature coefficient indicates that the preferred conformation is as shown in (**9**), analogous to that adopted by the isobutyl radical.[16] The substantially smaller value of $a(2H_\beta)$ shown by (**7**; R^1 = Bu^t, R^2 = H) suggests that the conformation (**10**) is now slightly preferred, as is the analogous conformation of the alkyl radical $Bu^tCH_2\dot{C}H_2$.[17] The long-range splitting of *ca.* 0.7 G from *one* proton observed in the spectrum of (**7**; R^1 = Me, R^2 = Bu^{t}CH$_2$) is presumably due to one of the two diastereotopic methylene protons in this sterically congested IRA.



(**9**)



(**10**)

Mechanistic Aspects.—The most plausible route for formation of the diazene radical anion (**1**) involves reaction of the azido radical with ammonia, as shown in equations (6)—(9). The

$$N_3^- \xrightarrow[\text{c.t.t.s.}]{h\nu} N_3^{\cdot} + e^-_{\text{amm.}} \qquad (6)$$

$$N_3^{\cdot} + NH_3 \rightleftharpoons \underset{\textbf{(11)}}{H_3N\dot{-}\bar{N}-\overset{+}{N}{\equiv}N} \qquad (7)$$

$$H_3N\dot{-}\bar{N}\dot{-}\overset{+}{N}{\equiv}N \longrightarrow H_3N\dot{-}N + N_2 \qquad (8)$$

$$H_3N\dot{-}N \longrightarrow H_2N-\dot{N}H \xrightarrow{-H^+} [HN{=}NH]^{-\cdot} \qquad (9)$$

adduct (**11**) contains a two-centre three-electron σ bond analogous to that linking nitrogen and halogen in the σ^* radicals $H_3N\dot{-}Cl$ and $H_3N\dot{-}Br$.[18] Loss of nitrogen from (**11**) could be accompanied or followed [equation (9)] by migration of hydrogen to give the hydrazyl radical, deprotonation of which affords the diazene radical anion.

On the basis of the results reported here it is not possible to define unequivocally the mechanism of IRA formation. A reasonable sequence of reactions, consistent with the experimental results, is shown in equations (10)—(14), but we

$$N_3^{\cdot} + R^1R^2C{=}CH_2 \rightleftharpoons \underset{\textbf{(12)}}{R^1R^2\dot{C}-CH_2N_3} \qquad (10)$$

$$R^1R^2\dot{C}-CH_2N_3 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\textbf{(13)}}{[R^1R^2C{=}CHN_3]^{-\cdot}} \qquad (11)$$

$$R^1R^2\dot{C}-CH_2N_3 \xrightarrow{-N_2} [R^1R^2\dot{C}-CH_2N] \longrightarrow \underset{\textbf{(14)}}{R^1R^2\dot{C}-C(H){=}NH} \qquad (12)$$

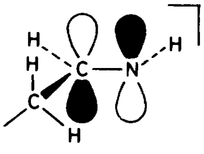
$$R^1R^2\dot{C}-C(H){=}NH \xrightarrow{+e^-} R^1R^2\bar{C}-C(H){=}NH \xrightarrow{+H^+} R^1R^2C(H)-C(H){=}NH \qquad (13)$$

$$R^1R^2C(H)-C(H){=}NH \xrightarrow{+e^-} [R^1R^2C(H)-C(H){=}NH]^{-\cdot} \qquad (14)$$

emphasise that alternative pathways are possible. In the presence of an alkene, addition of the electrophilic $N_3^{\cdot}$ to the C=C bond would compete with its capture by ammonia and the relative rates of addition should increase along the series $H_2C{=}CH_2 < RCH{=}CH_2 < R_2C{=}CH_2$ in accord with experiment. Reaction (10) is a propagation step in the homolytic addition of halogen azides to alkenes,[19] when the intermediate β-azidoalkyl radical (**12**) would go on to abstract halogen from N_3Hal. However, under our conditions other fates are possible for (**12**) and in a basic medium it could be reversibly deprotonated to give the vinyl azide radical anion (**13**), accounting for the isotopic exchange of D_α in the experiments with $(CD_3)_2C{=}CD_2$ in NH_3. The β-azidoalkyl radical could be less stable towards loss of nitrogen in ammonia than in less polar aprotic media and thermally or photochemically induced expulsion of N_2 from (**12**), accompanied or followed by hydrogen shift, would yield an α-iminoalkyl radical (**14**). Reduction (to give an enolate analogue) of (**14**), then protonation and further reduction, would give the IRA. A sequence analogous to equation (12) occurs during thermal or photochemical decomposition of an alkyl azide,[20] although (**12**) would have to lose nitrogen much more readily.

The result obtained with the trisubstituted ethene $Me_2C{=}CHMe$ is more difficult to accommodate, although the relatively long irradiation time necessary before the spectrum of (**2**) developed may indicate a more circuitous pathway for its formation. Loss of nitrogen and 1,2-shift of a methyl group rather than hydrogen[20] would eventually lead to the IRA $[Me_2C(H){-}C(H){=}NMe]^{-\bullet}$ (**15**), and it is unlikely that the e.s.r. spectra of (**2**) and (**15**) would be indistinguishable. However, in ammonia solvent it is possible that (**15**) could be rapidly converted into (**2**) by an amine-exchange reaction analogous to that which might be responsible for the absence of nitrogen hyperfine splitting in the spectra of the IRAs (see before).

Molecular Orbital Calculations.—In order to substantiate our conclusion, based on qualitative considerations (see before), that the nitrogen splitting for an IRA could reasonably be very small, we have carried out semi-empirical molecular orbital calculations for the ethanimine radical anion (**16**) at the MNDO–UHF level.[21] Optimisation of all geometrical variables gave a CC(H)NH skeleton which was very close to planar. The unpaired electron resides in a π* molecular orbital, as indicated in (**16**), and the π spin populations on carbon and nitrogen were 47 and 49%. respectively. After annihilation of quartet state contamination,[21] the calculated value of a(N) was small (+3.3 G) as expected. This calculation refers, of course, to an isolated radical anion in the gas phase; in ammonia solvent hydrogen bonding to nitrogen will occur and would be expected to result in a shift of spin density from nitrogen to carbon [stabilisation of (**8a**) relative to (**8b**)] with a consequent *decrease* in the already small value of a(N).



(**16**)

It is also noteworthy that the α-aminoalkyl radical $Bu^t{}_2\dot{C}N(H)SiMe_3$, in which the unpaired electron occupies a π* MO similar to that in an IRA, is also very small (1.3 G).[22]

Experimental

E.s.r. spectra were recorded during continuous u.v. irradiation of samples sealed in evacuated Suprasil quartz tubes, as described previously.[7] Sample tubes had internal diameters of 1.5 or 2 mm and were constructed with 5 mm i.d. side arms to facilitate mixing of the contents. The narrower tubes were used for solutions in neat ammonia; the wider tubes could be used when an ether co-solvent was present.

Liquified ammonia (B.D.H.) was treated with sodium metal under argon and the ammonia was then distilled from the blue solution into a steel storage cylinder. Dimethyl ether (B.D.H.) was used as received after passage of the gas through a short column of activated molecular sieves (4 Å). 1,2-Dimethoxyethane (Aldrich) was distilled from sodium and transferred to the sample tubes by trap-to-trap distillation on the vacuum line.

Sodium azide (B.D.H.) was dried by pumping at 35 °C and 0.01 Torr for 5 h and thereafter handled under dry argon. Tetra-n-butylammonium azide was prepared by the method of Brändström *et al.*[23] and dried by pumping at 35 °C and 0.01 Torr for 4 h. It is very hygroscopic and must be handled under dry argon at all times.

Undeuteriated alkenes were commercial products and were distilled from sodium prior to use. Perdeuterio-2-methylpropene was prepared by refluxing $[^2H_{10}]$-t-butyl alcohol (Aldrich) with an equal volume of 46% D_2SO_4 in D_2O. The alkene was carried in a slow stream of argon through a trap containing sodium hydroxide pellets and was then condensed in traps cooled to −78 °C. The alkene was dried over sodium and trap-to-trap distilled into a glass storage vessel sealed with a PTFE O ring greaseless vacuum tap (J. Young Ltd.). Mass spectroscopic analysis (12.5 eV) showed peaks at m/z 64 ($C_4D_8{}^{+\bullet}$), 63 ($C_4D_7H^{+\bullet}$), and 62 with relative intensities 95, 4, and 1, respectively.

Sodium 2-methylpropylate in 2-methylpropan-1-ol was prepared by dissolving sodium metal in the parent alcohol.

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