E.S.R. Evidence for the Rearrangement at 77 K of Ionized Allylamine to the Distonic Radical Cation $\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$

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The radical cation formed by radiolytic oxidation of prop-2-enylamine (allylamine) in Freon matrices at 77 K is the 3-iminiopropyl distonic species (3-iminium-1-propyl radical) resulting from a 1,2-hydrogen shift in the parent cation.

It is well known that nitrogen-centred amine radical cations undergo facile intramolecular 1,5-hydrogen transfer from carbon to nitrogen both in the gas phase[1—5] and in solution,[6—8] the thermodynamic driving force for this Hofmann–Löffler rearrangement (reaction 1) coming from the formation of a strong N–H bond in the substituted ammonium ion of the product.[9,10]

$$CH_3(CH_2)_3NH_2^{+\cdot} \rightarrow \cdot CH_2(CH_2)_3NH_3^+ \qquad (1)$$

Here we describe a different type of hydrogen migration in an unsaturated amine cation, the driving force in this case being supplied by the formation of a substituted iminium cation ($RCH{=}\overset{+}{N}H_2$) resulting from the 1,2-shift of a β-hydrogen atom to the γ,δ-unsaturated group.

As shown in Figure 1(a), the e.s.r. spectrum of the radical produced by radiolytic oxidation[11] of a solid solution of prop-2-enylamine (allylamine) in CF_3CCl_3 consists of a well-resolved 22.7 G† triplet of 16.9 G triplets, each triplet possessing the 1 : 2 : 1 intensity ratios characteristic of coupling to two equivalent hydrogens. Since the larger value of A (2H) is typical of α-hydrogen coupling in a carbon-centred radical, the spectrum can be assigned to an $RCH_2CH_2\cdot$ structure. This assignment implies that a rearrangement must have occurred from the nitrogen-centred radical cation $CH_2{=}CHCH_2\overset{+\cdot}{N}H_2$ formed initially, this species being the ground-state ion according to the results of photoelectron spectroscopy.[12] Clear evidence against a nitrogen-centred radical comes from comparative experiments in Freon matrices (CF_3CCl_3, $CFCl_3$, and $CF_2ClCFCl_2$) with both allylamine and *N*-dideuterio-allylamine, the radiolytic oxidation of these compounds yielding e.s.r. spectra which matched perfectly under the same experimental conditions, as exemplified by comparison of spectra (a) and (b) in Figure 1. Thus, deuterium labelling at the amine hydrogens has no effect on the e.s.r. spectrum that is obtained, contrary to expectation for a nitrogen-centred radical cation but consistent with a carbon-centred radical well removed from the amine group.

Further characterization of this radical was facilitated by our previous work[13] showing that the radical cation of cyclopropylamine rearranges to the ring-opened distonic radical cation $\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$. Since this species is isomeric with the allylamine radical cation and possesses the $RCH_2CH_2\cdot$ structure, it could also be the product of the allylamine radical cation rearrangement. In fact, the e.s.r. spectra of the radical cations derived from allylamine and cyclopropylamine are indistinguishable from each other in CF_3CCl_3 [Figure 1, (a) and (c)], $CF_2ClCFCl_2$ [Figure 2, (a) and (b)], and $CFCl_3$ (Table 1) when observed under identical conditions. This coincidence is all the more remarkable since the spectra in CF_3CCl_3 (Figure 1) have a very different appearance from those in $CF_2ClCFCl_2$ at low temperatures (Figure 2). Whereas this observation is difficult to reconcile with two different radicals always giving rise to accidentally equivalent spectra, these results are, of course, easily explained in terms of a common $RCH_2CH_2\cdot$ radical by a selective line-broadening effect in $CF_2ClCFCl_2$ (Figure 2) on the $M_I(2H_\beta) = 0$ components.[14]

Two other considerations strongly support the conclusion that the same signal carrier is produced from the allylamine and cyclopropylamine solutions. First, the magnitude of the β-hydrogen coupling (16.8—17.6 G, depending on temperature) in Table 1 is atypical for $RCH_2CH_2\cdot$ radicals,[15] so that fortuitous agreement between these couplings for two different radicals of this type is inherently unlikely. Secondly, we have observed the 80 G doublet e.s.r. spectrum of the propane-1-iminyl radical $CH_3CH_2CH{=}N\cdot$ at 110 K from irradiated allylamine solutions in the $CF_2ClCFCl_2$ matrix, paralleling the previous observation of this neutral radical from irradiated cyclopropylamine solutions in the same matrix.[13] The formation of this daughter radical from $\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$ in $CFCl_2CF_2Cl$ is attributable to the onset

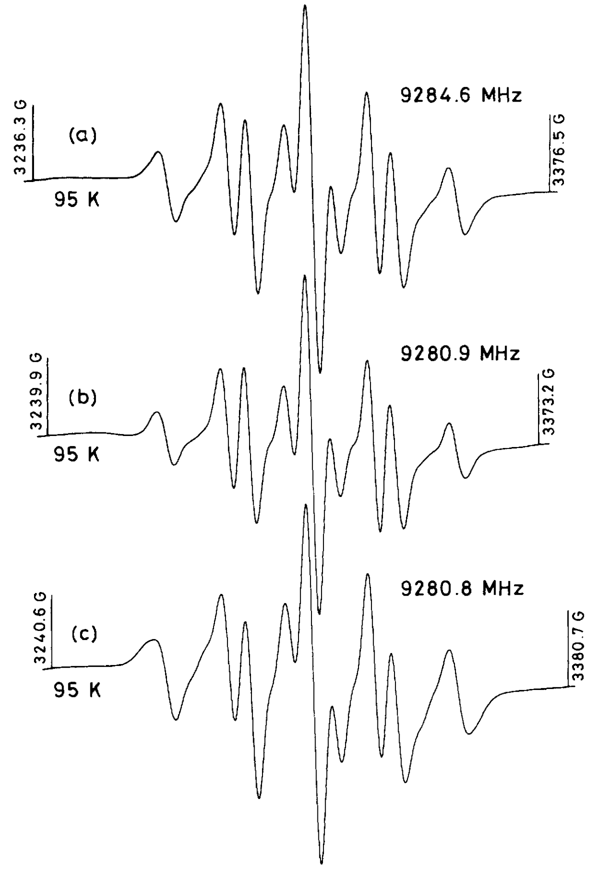

Figure 1. First-derivative e.s.r. spectra at 95 K of the radical cations produced by γ-irradiation at 77 K of dilute solid CF_3CCl_3 solutions of (a) allylamine, (b) [N-$^2H_2$]allylamine, and (c) cyclopropylamine.

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† 1 G = 10^{-4} T.

Table 1. E.s.r. parameters for the 3-iminiopropyl distonic radical cation produced by radiolytic oxidation of allylamine, [N-$^2H_2$]allylamine, cyclopropylamine, and [N-$^2H_2$]cyclopropylamine in Freon matrices.

Radical cation	Substrate	Solvent	T/K	Hyperfine couplings/G[a]		g_{iso}	Ref.
$\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$	$CH_2{=}CHCH_2NH_2$	CF_3CCl_3	140	22.6 ($2H_\alpha$),	17.4 ($2H_\beta$)	2.0027	This work
			95	22.7 ($2H_\alpha$),	16.9 ($2H_\beta$)	2.0026	This work
$\cdot CH_2CH_2CH{=}\overset{+}{N}D_2$	$CH_2{=}CHCH_2ND_2$	CF_3CCl_3	140	22.7 ($2H_\alpha$),	17.5 ($2H_\beta$)	2.0027	This work
			87	22.6 ($2H_\alpha$),	16.8 ($2H_\beta$)	2.0027	This work
$\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$	$CH_2{=}CHCH_2NH_2$	$CFCl_3$	150	22.6 ($2H_\alpha$),	17.2 ($2H_\beta$)	2.0026	This work
$\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$	cyclo-$C_3H_5NH_2$	CF_3CCl_3	140	22.6 ($2H_\alpha$),	17.6 ($2H_\beta$)	2.0026	This work
			95	22.6 ($2H_\alpha$),	17.0 ($2H_\beta$)	2.0027	This work
			80—140	22.6 ($2H_\alpha$),	17.0[b] ($2H_\beta$)	2.0026	13
$\cdot CH_2CH_2CH{=}\overset{+}{N}D_2$	cyclo-$C_3H_5ND_2$	CF_3CCl_3	130	22.6 ($2H_\alpha$),	17.4 ($2H_\beta$)	2.0027	This work
			100	22.5 ($2H_\alpha$),	17.1 ($2H_\beta$)	2.0026	This work
$\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$	cyclo-$C_3H_5NH_2$	$CFCl_3$	150	22.6 ($2H_\alpha$),	17.1 ($2H_\beta$)	2.0026	This work
			80—160	22.5 ($2H_\alpha$),	17.0 ($2H_\beta$)	2.0027	13

[a] 1 G = 10^{-4} T. [b] The slight temperature dependence of the β-hydrogen hyperfine coupling constant for $\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$ in CF_3CCl_3 observed in the present work was not reported in ref. 13.

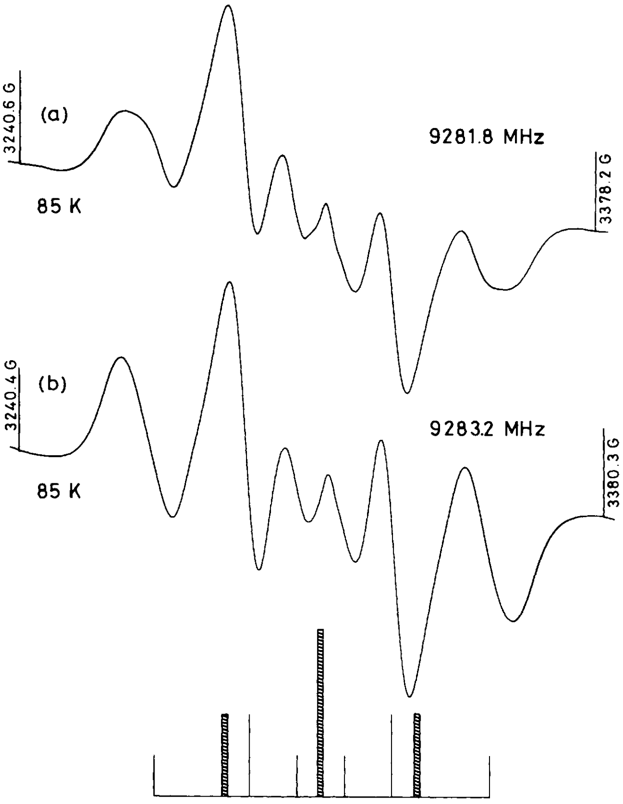
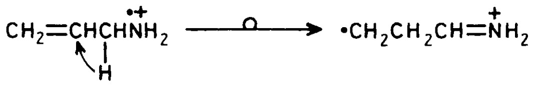


Figure 2. First-derivative e.s.r. spectra at 85 K of the radical cations produced by γ-irradiation at 77 K of dilute solid $CF_2ClCFCl_2$ solutions of (a) allylamine and (b) cyclopropylamine. The stick diagram reconstruction shows a triplet of triplets with the $M_I(2H_\beta) = 0$ lines [$A(2H_\beta) < A(2H_\alpha)$] represented by bars to indicate the broadening of these components in the low-temperature spectra. These spectra became better resolved at higher temperatures before the onset of ion–molecule reactions at 105 K (see text), all nine components (*cf.* Figure 1) being clearly observed under these conditions in each spectrum.

of ion–molecule reactions in this matrix, as discussed previously.[13] Therefore, the observation of the iminyl radical can be regarded as definitive evidence for the $\cdot CH_2CH_2CH{=}\overset{+}{N}H_2$ precursor in the allylamine solutions.

As shown in reaction (2), the rearrangement of the prop-2-enylamine radical cation (**1**) to the 3-iminiopropyl species (**2**) is readily formulated as a 1,2-hydrogen shift which leads to separated radical and cationic centres.



$$CH_2{=}CH\underset{H}{C}H\overset{\cdot+}{N}H_2 \xrightarrow{a} \cdot CH_2CH_2CH{=}\overset{+}{N}H_2 \quad (2)$$

(**1**) (**2**)

Since photoelectron spectroscopic studies[12] show that the positive hole is localized in (**1**) on the amine group, it seems remarkable at first sight that a β-hydrogen atom should be transferred to the relatively unperturbed π-bond which is nonadjacent to the amine cation. However, if the rearrangement is formally dissected into the two steps (**3a**) and (**3b**), it is apparent that this hydrogen shift is assisted in the early stage of the reaction by the nascent formation of the π bond in the emerging iminium cation.

Accordingly, the transition state energy for this 1,2-hydrogen shift should be lowered by the conjugation of the two partial π-bonds in the H-atom adduct of $CH_2{=}CHCH{=}\overset{+}{N}H_2$, the latter being isoelectronic with buta-1,3-diene. This conjugation replaces the weak homoallylic interaction between the nitrogen-centred cation and the olefin π-bond in the SOMO of the parent amine,[16] thereby facilitating the reaction. In agreement with our experimental results, calculations using the AM1 program[17] predict that for fully optimized geometries, (**2**) is more stable than (**1**) by 20.2 and 19.3 kcal mol^{-1} (cal = 4.184 J) for the *cisoid* and *transoid* CCCN planar structures, respectively.

Finally, the finding that the same distonic radical cation is produced by the ring opening of the cyclopropylamine cation and by the 1,2-hydrogen shift in the allylamine cation clearly points to the high stability of this distonic species, especially given the fact that the ionization occurs from a bonding orbital in cyclopropylamine[13] but from a nonbonding orbital in allylamine.[12]

$$CH_2{=}CHCH_2\overset{+\,\bullet}{N}H_2 \rightarrow CH_2{=}CHCH{=}\overset{+}{N}H_2 + H\cdot \qquad (3a)$$

$$CH_2{=}CHCH{=}\overset{+}{N}H_2 + H\cdot \rightarrow \cdot CH_2CH_2CH{=}\overset{+}{N}H_2 \qquad (3b)$$

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