Observation of Piperidine Aggregation and of Hydrogen–Proton Transfer between Piperidine Radical Cations and Piperidine Molecules in Freon Matrices. An ESR Study at Cryogenic Temperatures

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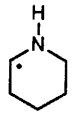
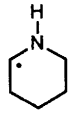
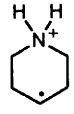
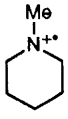
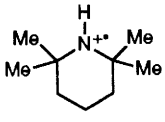
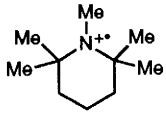
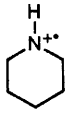
Piperidine forms small aggregates in most Freon matrices at cryogenic temperatures; upon X-irradiation, hydrogen–proton transfer between piperidine radical cations and piperidine molecules occurs.

Since publication of an incorrect interpretation of the ESR spectrum of pure piperidine irradiated at 77 K,[1] neither the piperidine radical cation nor the neutral piperidin-1-yl radical have been observed to our knowledge. Difficulties usually arise in the analysis of the ESR spectra of piperidine because of the superposition of at least two signals from different paramagnetic centres.[2] Here, we report ESR spectra of the piperidine radical cation and neutral piperidin-1-yl radical, trapped in different halocarbon matrices, and demonstrate direct evidence of the piperidine aggregation and hydrogen–proton transfer reactions both from the isothermal concentration dependence and from temperature-variation studies.

The piperidin-2-yl radical has been identified both in a γ-irradiated frozen aqueous piperidine solution at 243 K,[2b] and after electron irradiation of piperidine in a matrix of adamantane, thiourea or molecular sieve.[3] In the latter case more precise hyperfine coupling constants (hfc) have been revealed (Table 1). A rapid inversion of the boat conformer, exchanging the axial and equatorial hydrogens of the methylene groups adjacent to the N-atom and the radical C-atom, was observed in the temperature range 203–343 K.[3] Cationic piperidine-4-yl radicals ($\cdot\overline{CH–CH_2–CH_2–NH_2^+–CH_2–CH_2}$) have been generated in aqueous solution of piperidine by reaction with ·OH at low pH.[4] The authors concluded that at 278–313 K the radical formed from piperidine undergoes chair–chair ring-flipping with rate constants in a range intermediate between fast and slow exchange, and the activation energy E_a for this interconversion is *ca.* 7.3 kcal mol^{-1} (1 cal = 4.184 J).[4] It is noteworthy that Trifunac and coworkers have recently observed substituted piperidine cation radicals (2,2,6,6-tetramethylpiperidine, 1,2,2,6,6-pentamethylpiperidine) in liquid n-hexane using the highly sensitive and selective time-resolved fluorescence-detected magnetic resonance (FDMR) technique, but they failed to observe piperidine and 2,6-dimethylpiperidine cation radicals.[5] They proposed proton transfer [eqn. (1)] and H-atom

Table 1 ESR parameters for radicals related to the present study

Radical cation or radical	Solvent	T/K	g	Hf couplings (G)	Ref.
	Adamantane	203		$a(^{14}N) < 1.95, a(1H_{\alpha}) = 13.5$ $a(1H_{\beta}) = 42.2, a(1H_{\beta'}) < 1.95$ $a(H_N) = 6.7, a(1H_{\gamma}) = 6.7$ $a(1H_{\gamma N}) < 1.95$	3
		343		$a(^{14}N) < 1.95, a(1H_{\alpha}) = 13.8$ $a(2H_{\beta}) = 19.4, a(H_N) = 6.9$ $a(2H_{\gamma N}) = 3.5$	3
	H_2O–piperidine (17 : 1)	77		Unidentified	2
		243		$a(1H_{\alpha}) = 15, a(1H_{CH2}) = 40$	2
	Acid solution	RT[a]		$a(1H_{\alpha}) = 21.9, (a_{ax} + a_{eq})$ $(4H_{\beta}) = 48.9$[b]	4*a*
	Acid solution	295		$a(1H_{\alpha}) = 21.8, a(2H_{\beta}) = 39.4$ $a(2H_{\beta'}) = 9.4$[c]	4*b*
	$CFCl_3$	77		$a(3H_{Me}) = 29, a(2H_{\beta}) = 38$ $a_{\|}(^{14}N) = 48, A_{\perp}(^{14}N) = 0 + 4$	7*a*
	n-Hexane[d] 10^{-4} mol dm^{-3} [$^2H_{10}$]anthracene	205		$a(^{14}N) = 18.6, a(1H_N) = 21.3$	5
	n-Hexane[d] 10^{-4} mol dm^{-3} [$^2H_{10}$]anthracene	290		$a(^{14}N) = 21, a(3H_{NMe}) = 28$	5
	$CF_3C_6F_{11}$	77	2.0035	$a(1H_N) = 26, a(2H_{\beta}) = 33$ $a(2H_{\beta'}) = 6.5, A_{\|}(^{14}N) = 42$ $A_{\perp}(^{14}N) = 7.5$	This work
	$CFCl_3$	77	$g_{\perp} = 2.0051$ $g_{\|} = 2.0035$	$a(2H_{\beta}) = 34, a(2H_{\beta'}) = 5.5$ $A_{\|}(^{14}N) = 39.5, A_{\perp}(^{14}N) = 1.5$	This work

[a] Room temp. [b] Chair–chair interconversions. [c] A conformational interconversion rate constant is 2.5×10^9 s^{-1}. [d] Time-resolved fluorescence-detected magnetic resonance (FDMR) technique.

abstraction [eqn. (2)] bimolecular reactions of the aminium cation radicals with neutral parent molecules as possible reasons of the failure to observe the latter cation radicals.

$$R_2NH^{\cdot+} + R_2NH \rightarrow R_2N^{\cdot} + R_2NH_2^{+} \quad (1)$$

$$R_2NH^{\cdot+} + R_2NH \rightarrow R_2NH_2^{+} + R_2N^{\cdot} \quad (2)$$

The products of the hydrogen-atom or proton-transfer reactions cannot be detected by the FDMR since only ESR signals of ion–radical pairs are in the FDMR spectra. They proposed also that in the case of tetra- and penta-methylpiperidines steric effects can restrict those bimolecular reactions and the lifetime of the cation radicals becomes sufficiently long to observe them by FDMR.[5]

In previous papers the electronic structure and molecular dynamics of the pyrrolidine and azetidine radical cations and the deprotonated neutral 1-aminyl radicals were investigated by ESR spectroscopy and *ab initio* calculations.[6] Cation radicals of the former amines could be stabilized with ease in all Freon matrices used at sufficiently low concentrations of solute (*ca.* 1.0 mol%). Neutral 1-aminyl radicals have been observed in matrices that form frozen glasses at 77 K ($CF_2ClCFCl_2$, CF_2ClCF_2Cl) above the phase-transition temperatures (*ca.* 95 K). This can be explained by the bimolecular hydrogen–proton transfer reactions discussed above [eqns. (1) and (2)].

This communication is concerned with the six-membered cyclic amine piperidine. At very low concentrations of piperidine (*ca.* 0.04 mol%, which is on the limit of the sensitivity of the technique) a broad poorly resolved ESR signal was observed in all of the chlorofluorocarbon matrices

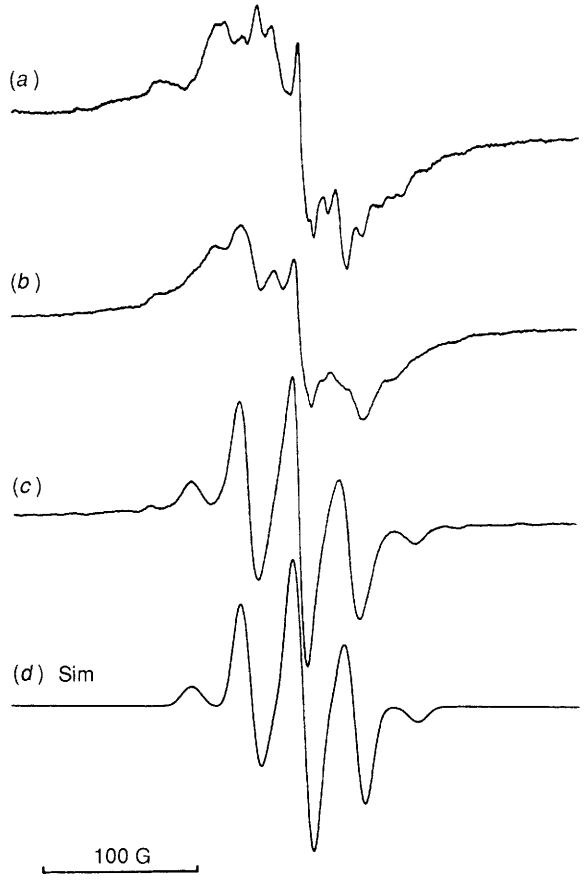


Fig. 1 First-derivative ESR spectra obtained for piperidine at (*a*) 0.04 mol%, (*b*) 1.4 mol% and (*c*) 10 mol% in $CFCl_3$ at 77 K after irradiation for 5 min with an X-ray tube having a tungsten anode operating at 70 kV and 20 mA. Spectrum (*c*) is attributable mainly to the piperidin-1-yl neutral radical and can be simulated (*d*) using the parameters in Table 1, the linewidth being 9 G (Gaussian lineshape) (1 G = 10^{-4} T).

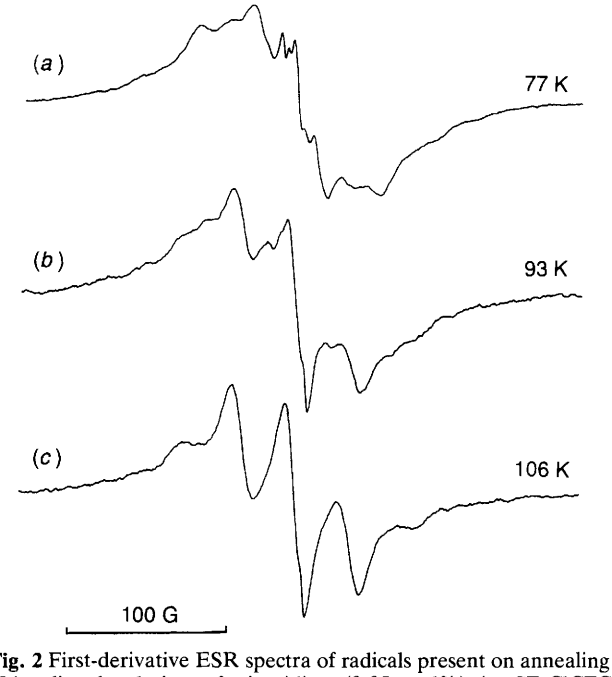


Fig. 2 First-derivative ESR spectra of radicals present on annealing a X-irradiated solution of piperidine (0.05 mol%) in $CF_2ClCFCl_2$ between 77 and 106 K. Spectra are the superposition of signals from the piperidine radical cation and the piperidin-1-yl radical (see the text), while spectra (*b*) and (*c*) show the growth of the piperidin-1-yl radical accompanied by the decay of the piperidine radical cation.

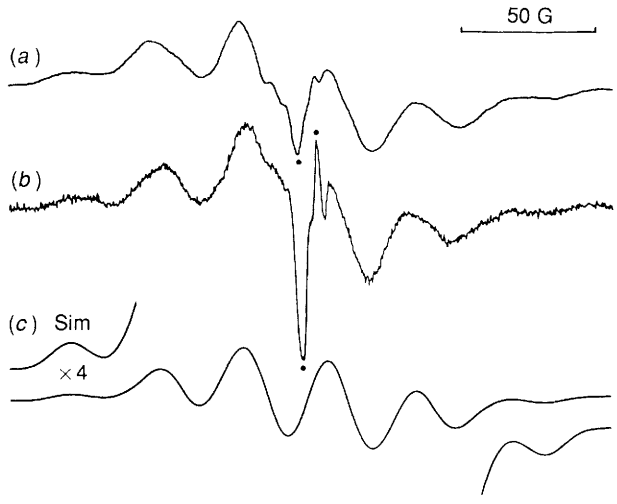


Fig. 3 First-derivative ESR spectra attributed to the piperidine radical cation: (*a*) The result of a subtraction of the high temperature spectrum of piperidine in $CF_2ClCFCl_2$ [Fig. 2(*c*)] from the low temperature one [Fig. 2(*a*)] with the relative weight 0.7 : 1.0; (*b*) experimental ESR spectrum obtained for CF_3c-C_6F_{11} containing 1 mol% piperidine after X-irradiation at 77 K (• indicates a background signal). (*c*) The simulated spectrum was computed using the parameters in Table 1, the linewidth being 10 G (Gaussian lineshape).

employed [Fig. 1(*a*) and 2(*a*)].† Such a spectrum might appear when two different paramagnetic species with equal (or close) hfc but with odd and even numbers of equivalent nuclei simultaneously are present in the sample with equal weight. It is known that a proton attached to the N-atom has rather large hfc in the amine cation radicals (*ca.* 25 G,‡ pyrrolidine cation radical[6a,c]), which is comparable to the hfc of the two axial β-protons in the ring (*ca.* 38 G, *N*-methylpiperidine cation radical[7a]). In the case of a neutral nitrogen-centred radical there are only two β-protons with the hfc close to that of the cation radical. Here, it is proposed that the broad singlet is the superposition of signals from the piperidine cation and neutral piperidine-1-yl radicals. This is supported by isothermal concentration studies in the $CFCl_3$ matrix and the temperature-variation experiments in the $CF_2ClCFCl_2$ matrix, to be explained as follows: Fig. 1 represents the transformation of the ESR spectra of the X-irradiated piperidine in $CFCl_3$ following an increase of the solute concentration. The features from the cation species disappeared gradually while the lines of the neutral radical grew at the same time. At a piperidine concentration of *ca.* 10 mol% the neutral radical became dominant [Fig. 1(*c*)]. The latter spectrum, attributed to the piperidin-1-yl radical, can be simulated with the following hfc: a(2H) = 34 G, a(2H) = 5.5 G, $A_\perp(^{14}N)$ = 1.5 G and $A_\parallel(^{14}N)$ = 39.5 G, using a Gaussian line shape with line width (lw) = 9.0 G [Fig. 1(*d*)]. The broad lines on the wings of the spectra are probably due to the matrix radicals. Fig. 2 shows the irreversible spectral change, which occurred during the annealing from 77 to 106 K of a sample containing *ca.* 0.05 mol% piperidine in $CF_2ClCFCl_2$.

These spectra almost coincide with those presented in Fig. 1. A set of subtractions of the high temperature spectrum [Fig. 2(*c*)] from the low temperature one [Fig. 2(*a*)] has been made and the result with the relative weight 0.7 : 1.0 is presented in [Fig. 3(*a*)]. The latter is very similar to the ESR spectrum of the piperidine in CF_3c-C_6F_{11} irradiated and measured at 77 K [Fig. 3(*b*)]. This spectrum is here attributed to the piperidine

† We report here only results in $CFCl_3$ and $CF_2ClCFCl_2$ matrices. Similar spectra of the piperidine irradiated and measured at 77 K were observed in CF_3CCl_3 and CF_2ClCF_2Cl.

‡ 1 G = 10^{-4} T.

cation radical and can be simulated with the following hfc: a(1H) = 26 G, a(2H) = 33 G, a(2H) = 6.5 G, $A_{\perp}$(14N) = 7.5 G, $A_{\|}$(14N) = 42 G, using a Gaussian line shape with lw = 10.0 G [Fig. 3(*c*)]. On the basis of these results we conclude that: (*i*) in contrast to alkanes, which form small aggregates only in $CFCl_3$,[8] piperidine tends to form clusters in almost all Freon matrices used in the studies; (*ii*) aggregation of piperidine in perfluoroalkanes does not occur; (*iii*) hydrogen–proton transfer between piperidine radical cations and piperidine molecules occurs; (*iv*) the 'reaction volume' model[9] in the rigid matrices should be considered while diffusion-controlled ion–molecule reactions take place in $CF_2ClCFCl_2$ giving the same radical products.[6,7b,10] The same conclusions have been reached by Qin and Williams concerning aziridine.[7b] These results are puzzling and a pertinent question is: why do some cyclic amines tend to form clusters (aziridine, piperidine), but not others (pyrrolidine, azetidine)? A possibility to clarify this would be to extend the study to involve partially deuteriated as well as methylsubstituted piperidines. Work along these lines is in progress and the results will be published elsewhere.

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