ESR AND OPTICAL STUDIES ON THE CATION-RADICAL OF PYRIDINE IN A γ -IRRADIATED RIGID MATRIX AT LOW TEMPERATURES

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Evidence for the cation-radical of pyridine is obtained by LSR and optical studies of γ -irradiated frozen solutions of pyridine in trichlorofluoromethane at 77 and 4 K. The cation-radical is a *a*-type radical, the positive charge residing mostly in the nitrogen kone pair orbital. Consistent spectral data are obtained also for 2-deutero-, 4-deutero-, 2,6-dideutero-, and perdeutero-pyridines.

1. Introduction

Despite the importance of pyridine as the prototype of azaaromatics uncertainty shrouded until recently as to the assignment of the first two vertical ionizations [1]. This is due to the fact that the first π orbital lies accidentally close to the lone pair orbital [1-3]. The fact entails the difficulty in predicting the nature of the cation-radical of pyridine. An attempt to identify the cation-radical by ESR was made some time ago [4,5]. Ionization of polycrystalline pyridine at 77 K by γ -irradiation, however, resulted in the formation of 2-pyridyl radical apparently by the following reaction,

$$\bigcirc^{\mathsf{N}^+} + \bigcirc^{\mathsf{N}} \to \bigcirc^{\mathsf{N}^+} + \bigcirc^{\mathsf{N}^+} .$$
 (1)

Since the cation-radicals of various N-heteroaromatics were obtained successfully in a γ -irradiated Freon mixture at 77 K [6], it was expected that the cationradical of pyridine also might be produced in the same matrix. However, it turned out that the ESR spectrum of the γ -irradiated pyridine—Freon mixture at 77 K differs little from the spectrum of the Freon mixture alone. Therefore it had to be concluded that the irradiation did not produce the paramagnetic cationradical of pyridine.

It is found, however, that pyridine in trichlorofluoromethane at 4 K gives an ESR spectrum attributable to a σ -type cation-radical of pyridine with an isotropic hyperfine coupling constant of nitrogen of 41 G. The optical absorption spectrum of the pyridine cation is also consistent with the photoelectron spectrum of pyridine [1]. The present work exemplifies the potential usefulness of trichlorofluoromethane as a matrix for the production of elusive cation-radicals like that of pyridine.

2. Experimental

Reagent grade pyridine from Wako Pure Chemical Ind., was purified first by distillation, and then by complexation with zinc chloride which was decomposed by sodium hydroxide to reproduce pyridine. Perdeuterated pyridine was purchased from CEA and used as received. 2-deutero-, 4-deutero- and 2,6-dideutero-pyridines were synthesized by the method in the literature [7]. NMR spectra of each isotopically substituted pyridine showed no trace of impurities. Trichlorofluoromethane (TCFM) and 1,1,2,2,-tetrafluoro-1,2-dibromoethane (TFDBE) from Daikin Kogyo were used without purification. Preliminary tests using distilled Freons showed no effect of the distillation.

About 20 mM of pyridines was dissolved in TCFM or in an equivolume mixture of TCFM and TFDBE (the mixture will be called FM standing for Freon mix-

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ture). evacuated in Suprasil cells of 3 mm outer diameter. The sample was irradiated in liquid helium or in liquid nitrogen, and the ESR signal was measured at the same temperatures employing a JEOL FE spectrometer. For optical measurements samples were sealed in a 1.5 mm or 0.5 mm thick Suprasil cell and the absorption before and after irradiation was measured by a Cary 17I spectrophotometer.

3. Results and discussion

 γ -irradiation of pure glassy FM at 77 K induces an optical absorption band of $\lambda_{max} = 560$ nm which is attributed to the radiation-induced positive ions of the Freons [6,8]. When solutes of low ionization potentials are present in FM, the positive charge is scavenged by the solutes and absorption due to the solute cations appears at the expense of the absorption at $\lambda_{max} =$ 560 nm [6.8]. Since a new absorption at $\lambda_{max} = 390$ nm appeared in the solution of pyridine in FM, the absorption was regarded, in a previous paper [8], as due to the cation-radical of pyridine. However, it is found that the ESR spectrum of the same system does not indicate the formation of the cation-radical of pyridine because there is no significant difference between the pyridine-FM and the pure FM systems as demonstrated in figs. 1a and 1b. The spectra in figs. 1a and 1b are typical of fluorine-containing radicals [9] produced by reactions such as

$$CFCl_3 + e^- \rightarrow \cdot CFCl_2 + Cl^-, \qquad (2)$$

$$CF_2BrCF_2Br + e^- \rightarrow \cdot CF_2CF_2Br + Br^-.$$
 (3)

The counterpart positive ions of the Freons may not be clearly seen if the positive charge is localized on the nearly degenerate lone-pair orbitals of halogens [10]. The absence of an ESR signal attributable to the cation-radical of pyridine implies that the charge is not transferred to pyridine despite the optical change from $\lambda_{max} = 560$ nm to 390 nm. Possible reconciliation is that although the positive charge in the Freon molecules migrates to pyridine the charge is not transferred to pyridine but a charge-transfer complex is produced in which the charge is mostly localized in one of the Freon molecules adjacent to the pyridine molecule.

However, when TCFM is used as a matrix, the ESR spectra of pure TCFM and of all five pyridines in



Fig. 1. ESR spectra of FM and TCFM solutions with and without pyridine or pyridine- d_5 irradiated and measured at 77 K. The amplification for (a) and (b) is the same, and that for (c). (d), and (e) is the same. The former is about 15 times as large as the latter. Radiation doses for all five are the same.

TCFM solutions are remarkably different as figs. 1c and 1d show representatively for pyridine- h_5 and $-d_5$, respectively. The three spectra of figs. 1c-le are obtained with the same dose and the same signal amplification. The relatively weak "background" signal of pure TCFM in fig. 1e is attributable to the fact that the radical in reaction (2) contains the fluorine atom whose anisotropic hfc constants are large enough to obliterate the ESR signal [9]. This feature is favorable for the detection of relatively sharp signals due to organic radicals such as the pyridine cation. The characteristic complexity of the spectrum of pyridine- h_5 in TCFM is reminiscent of the spectrum of the phenyl radical which is isoelectronic with the o-type cation of pyridine. The relatively broad spectrum for an organic radical spanning about 150 G immediately suggests that the positive charge is successfully transferred to pyridine, as

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$$\operatorname{CFCL}_{3}^{+} + \bigcup^{\mathbb{N}} \longrightarrow \operatorname{CFCL}_{3} + \bigcup^{\mathbb{N}^{+}} (4)$$

and that the odd electron in the pyridine cation resides mostly in the nitrogen lone-pair orbital. The complexity of the ESR spectrum decreases gradually as the protons were deuterated, but the broad triplet feature remains as is especially evident for the spectrum of pyridine- d_5 in TCFM.

In order to confirm the assignment of the cation, an ESR simulation was attempted referring to the work of phenyl radical [11]. However, despite repeated trials of parametrization the simulated spectra did not agree with the observed one to a satisfactory degree. In particular, the outer two peaks of the broad triplet were systematically larger than the simulation, suggesting either the formation of byproducts or lineshape distortion due to some interaction of the pyridine cation with matrix molecules or due to some molecular motion of the cation. Therefore, in order to eliminate or reduce these ambiguities, irradiation and measurement of the samples at 4 K was attempted to obtain the following results.

(1) The superposing signals are suppressed and the general agreement with the simulation is improved as shown in fig. 2.

(2) The ESR signals are very sensitive to microwave power saturation, and the power has to be reduced to the order of 100 pW to obtain reproducible and undistorted spectra.

(3) When the samples irradiated at 4 K are warmed to 77 K, the spectrum agrees with that of the samples irradiated and measured at 77 K.

(4) When the samples irradiated at 77 K are cooled to 4 K, the spectrum remains unchanged.

The irreversible temperature effects rule out the possibility of the presumed molecular motion. The spectral change and the remarkable difference in saturation between 4 K and 77 K may be accounted for in the following way. By analogy with the trapped electron in matrices at 4 K and 77 K [12], the pyridine cation may reorientate irreversibly the surrounding TCFM molecules in the softened matrix at 77 K so that the lone-pair electrons of the TCFM molecules may interact with the pyridine cation more easily than in the rigid matrix at 4 K. Such an interaction may cause an efficient relaxation of the spin system and a change in spectral line shape.



Fig. 2. ESR spectra of TCFM solutions containing various pyridines. Left column: irradiated and measured at 4 K. Right column: simulated with the parameters for $C_6H_5N^*$ in table 1. For the deuteron the parameters in table 1 are reduced accordingly.

Even at 4 K the agreement between the observed and simulated spectra in fig. 2 is not complete. However, considering the fact that the cation is in a complex polyatomic molecular matrix easily electronically polarisable by the positive charge of the cation and that a multitude of parameters is involved, the general agreement with a common set of the parameters for all the pyridine isomers should be taken positively rather than negatively. (Note that the better agreement in the work of phenyl radical [11] should partly be attributed to the inert matrix of rare gas solids.) The best-fit parameters used for the simulation in fig. 2 are compiled in table 1. It should be remarked that the isotropic hfc constant of nitrogen amounts to 41 G which is higher than that for the well studied 2-pyridyl radical [5]. It is also interesting to note that the isotropic hfc constants of ortho and para hydrogens are much larger than those of the closely related phenyl radical whose values are $a_{iso,ortho} = 17.4$, $a_{iso,meta} =$

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ESR parameters of the cation-radical of pyridine as determined from the simulation. Numbers in parentheses represent the calculated values in gauss units. θ (in degree) represents the angle of rotation of coordinates for the principal values of the hyperfine coupling constants *a* (in gauss) relative to the coordinate system, *x* and *y*. An example of θ is depicted for the ortho proton in the inset

	g _{av} = 2.0032 ^a iso	$g_x = 2.0033$ a_x	g _y = 2.0026 a _y	$g_{z} \approx 2.0037$ a_{z}	
N	41.0 (51.8)	-12.4 (-9.5)	22.4 (16.9)	-10.0 (-7.4)	0.0
Hortho	29.3 (17.8)	5.4	-2.4	-3.0	160
Hmeta	8.6 (5.7)	2.0	-0.9	-1.1	0.2
Hpara	11.2 (11.9)	0.1	0.1	-0.2	0.0

5.9, $a_{iso,para} = 1.9 G [11]$. The initial guess for the isotropic hfc constants was estimated by an INDO calculation, and is included in table 1. They agree with the final parameters obtained by simulation within roughly 30% except for the case of ortho hydrogens. This seems to imply an extra cause of spin delocalization between nitrogen and the adjacent hydrogens. The main spectral pattern of the triplet was reproduced for all pyridines with $a_{N,iso} = 41$ G. A few percent variation around this value could reproduce the main feature which means that $a_{iso,N}$ lies within the range of 40 to 43 G. The anisotropic hfc constants of nitrogen were estimated by using the McConnell-Strathdee relation in combination with the INDO MO's and were improved by repeated curve fittings [13]. The principal values of the A tensor of nitrogen attained in this way are also in agreement with the initial calculated values within 30%. The anisotropies of the proton hfc constants were found small and the parameters in table 1 were chosen on the basis of general agreement of the spectrum. The anisotropy of the g factor was estimated by a standard procedure with reference to the photoelectron spectrum of pyridine for the orbital energies [1]. The general pattern of simulated spectra remained more or less the same against the change of calculated g tensors in the vicinity of the values listed in table 1.

The assignment of the σ -type cation also accounts for the observed optical spectra of pyridine—TCFM systems as shown in fig. 3: Although the system freezes to an opaque polycrystalline solid, the absorption spectra could be measured with the thickness of samples reduced to 0.5 mm. The spectra in fig. 3 are obtained as the difference of absorptions before and after irra-



Fig. 3. Optical spectrum of pyridine cation (upper) and photoelectron spectrum of pyridine (lower). The solid and the dotted curves in the optical spectrum represent the spectra of pyridine in TCFM and TCFM alone, respectively. Both are irradiated to the same radiation dose, therefore the absorbances indicate the relative intensities of the pyridine cation (solid curve) and the "background" signal (broken curve).

diation at 77 K to the same dose for the samples with and without pyridine. Contrary to the ESR spectra of the various pyridines the optical spectra are almost identical among the pyridines studied as they should be. The optical spectra at 4 K were not measurable due to a technical reason, but the spectra at 77 K in fig. 3 may be considered to impart essential features of the cation despite the assumed weak interaction of the cation with the matrix. Then, the optical spectra are compatible with the photoelectron spectrum of pyriVolume 68, number 1

dine because the two optically allowed transitions at about 2.6 and 4.1 eV predictable from the photoelectron spectrum seem to correspond to the optical absorption bands at $\lambda_{max} = 450$ nm and 310 nm.

A question remains why the pyridine embedded in TCFM is oxidized to its genuine cation by the charge transfer while in the Freon mixture the positive charge cannot overcome the barrier between the matrix molecules and the pyridine molecule. Since the ionization potentials of TCFM, TFDBE, and pyridine are reported as 11.8, 11.4, and 9.6 eV, respectively [1,14], the exothermicities of the charge transfer from matrix to pyridine are 2.2 eV for pyridine-TCFM systems and 1.8 eV for pyridine-FM systems (in Freon mixture the charge is assumed to migrate between TFDBE molecules since the ionization potential is lower than that of the other component). It is not clear whether or not this difference in the excess energy is decisive in the successful charge transfer to pyridine. In any case it seems that the charge transfer in the present systems is an all-or-none process depending on the nature of the matrix molecule.

In conclusion, the choice of TCFM and the temperature of 4 K has led to the detection of the elusive pyridine cation and the cation is characterized by the ESR parameters compiled in table 1.

References

 R. Gleiter, E. Heilbronner and V. Hornung, Helv. Chim. Acta 55 (1972) 255.

- [2] W. von Niessen, G.H.F. Diercksen and L.S. Cederbaum, Chem. Phys. 10 (1975) 345.
- [3] J.O. Berg, D.H. Parker and M.A. El-Sayed, Chem. Phys. Letters 56 (1978) 411.
- [4] K. Tsuji, H. Yoshida and K. Hayashi, J. Chem. Phys. 45 (1966) 2894.
- [5] H.J. Bower, J.A. McRae and M.C.R. Symons, J. Chem. Soc. A (1968) 2696.
- [6] T. Kato and T. Shida, J. Am. Chem. Soc., to be published.
- [7] B. Bak, L. Hansen and J. Rastrup-Andersen, J. Chem. Phys. 22 (1954) 2013.
- [8] A. Grimison and G.A. Simpson, J. Phys. Chem. 72 (1968) 1776.
- [9] R. Lontz and W. Gordy, J. Chem. Phys. 37 (1962) 1357;
 R.J. Cook, J.R. Rowlands and D.H. Whiffen, Mol. Phys. 7 (1963) 31;
 M. Iwasaki, K. Toriyama and B. Eda, J. Chem. Phys. 42 (1965) 63.
- [10] S.P. Mishra and M.C.R. Symons, J. Chem. Soc. Perkin II (1975) 1492.
- [11] P.H. Kasai, E. Hedaya and E.B. Whipple, J. Am. Chem. Soc. 91 (1969) 4364.
- [12] H. Hase and T. Warashina, J. Chem. Phys. 59 (1973) 2152.
- [13] O. Edlund, A. Lund, M. Shiotani, J. Sohma and K.A. Thuomas, Mol. Phys. 32 (1976) 49.
- [14] T. Cvitas, H. Gusten and L. Klasinc, J. Chem. Phys. 67 (1977) 2687;
 H.J.T. Preston and J.J. Kaufman, Chem. Phys. Letters 50 (1977) 157.