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ESR Spectrum of Bromopyridines Irradiated with Ultraviolet Light. Confirmation of Pyridyl Radical Formation in Irradiated Pyridine and Their Formation Mechanism

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When pyridine was irradiated with electron beams or γ rays, there was observed the three line ESR spectrum with a coupling constant of about 30 gauss at -196°C.[1-5] Although this spectrum was attributed initially to pyridine cation radicals,[1-3] Symons *et al.*[4,5] attributed the spectrum to 2-pyridyl radicals mainly on the basis of observation of a large coupling constant of ^{13}C. The intensity of the ^{13}C signal, however, was not mentioned. The present investigation was carried out in order to confirm this assignment and to discuss about their formation mechanism.

It is well known that carbon-halogen bonds are easily broken homolitically by ultraviolet irradiation. Therefore it is expected that photolysis of halogenated pyridines will produce corresponding pyridyl radicals. Three isomers of bromopyridines were photolized and ESR spectra were recorded.

Experimental

Commercial 2- and 3-bromopyridines were used without further purification. 4-Bromopyridine was received as a hydrochloride and was used as it was. These samples were photolized in an ESR cavity by ultraviolet light from a Xenon short arc lamp (Ushio Electric Inc. UXL-500D) at -196°C. ESR measurements were carried out at -196°C with an X-band ESR spectrometer with 100 Kc field modulation. (Japan Electron Optics Lab. Co., Model JES, 3BS-X)[6]

Results and Discussion

After 2-bromopyridine was photolized at -196°C for 60 min, an ESR spectrum shown in Fig. 1a was observed, which is a three-line spectrum with a coupling constant of about 30 gauss. This spectrum is almost identical with that observed for pyridine irradiated with ionizing radiation.[1-5]

On the other hand 3- and 4-bromopyridines irradiated with ultraviolet light gave apparent singlet spectra with total line widths of about 66 and 60 gauss, respectively, as shown in Figs. 1b and c.

The fact that the triplet spectrum was obtained from only 2-bromopyridine leads to the conclusion that this hyperfine structure is caused by interaction of unpaired

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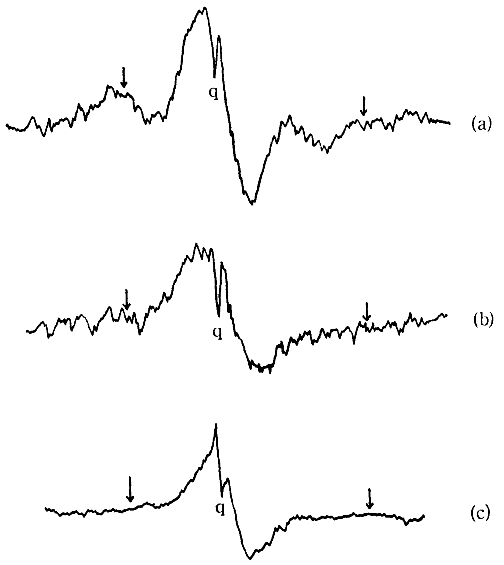
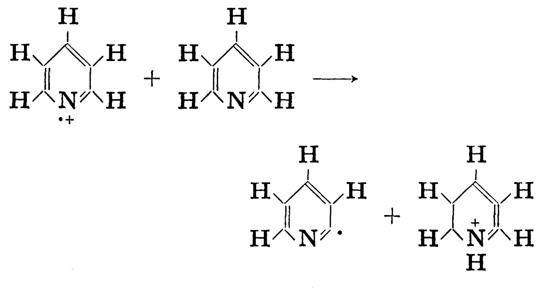


Fig. 1. ESR spectra of bromopyridines irradiated with ultraviolet light at −196°C for an hour.
a) 2-bromopyridine, b) 3-bromopyridine, and c) 4-bromopyridine hydrochloride
Arrow marks represent the positions of Mn^{2+} absorptions. Distance between these two marks is 86.7 gauss.
q represents a quartz signal.

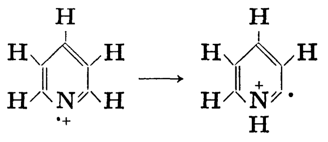
electrons with a nitrogen nucleus, and that the free radicals responsible for the ESR spectrum are 2-pyridyl radicals as expected, although the apparent intensity ratio of the triplet spectrum is not exactly 1 : 1 : 1, probably because of superposition of the spectrum due to the second radicals (II) described in the previous paper.7) The line widths of the singlet spectra observed for 3- and 4-bromopyridines seem to be reasonable for corresponding pyridyl radicals since a close value is expected for the phenyl radicals8,9) when the worse resolution of the spectrum is assumed. Therefore it is clear that the 2 pyridyl radical shows the three-line spectrum with a coupling constant of about 30 gauss. Consequently assignment of the ESR spectrum of pyridine irradiated with ionizing radiation at −196°C mainly to the 2-pyridyl radicals is thought to be reasonable.

This pyridyl radical produced in pyridine irradiated with ionizing radiation, however, does not seem to be produced by direct hydrogen atom abstraction from the position-2. The primary process of radiation is ionization of electrons in the nonbonding orbital of the nitrogen nucleus.1) Cation radicals thus formed could be precursors of the 2-pyridyl radicals, that is consistent with the fact that pyridine hydrochloride10) and the pyridine complexes with metal salts7) did not give the pyridyl radicals after γ-irradiation, where lone pair electrons of the nitrogen nucleus are no longer available for ionization. This is also supported by the fact that ultraviolet photolysis of the pyridine-iodine complex with the light corresponding to the charge transfer band of the complex gave the same spectrum even though the intensity is small, since photoexcitation of the complex will produce primarily pyridine cation radicals through the excited state.2)

Symons *et al.*5) suggested the 2-pyridyl radicals can be formed by the loss of a proton as follows:


(1)

There is, however, another possibility to produce 2-pyridyl radicals (although they are of protonated form) from pyridine cation radicals, that is, isomerization of pyridine cation radicals.


(2)

The protonated pyridyl radical has an extra proton on a nitrogen atom. Although the splitting due to this proton may be expected, the value will be too small to give the splitting in the similar way to the ring proton on position 3.5) If this is correct, the protonated form can give the similar spectrum to that of unprotonated pyridyl radicals.

These two possible structures of free radicals (protonated- and unprotonated-forms) are quite similar to those of free radicals in irradiated 2-methyltetrahydrofuran.11)

The protonated form is isoelectric with phenyl radical. Phenyl radicals produced by irradiation seem to be unstable even at −196°C since the ESR spectrum due to phenyl radicals was hardly observed at −196°C in benzene irradiated with ionizing radiation, although their formation is expected as donors of hydrogen atoms to form cyclohexadienyl radicals.12) The situation is the same for protonated pyridyl radicals in irradiated pyridinium ions.10) Therefore protonated form might be less stable than unprotonated one. The same conclusion could be drawn by comparison of resonance energies of pyridine (43 kcal/mol) and benzene (40 kcal/mol). Therefore according to this stability consideration, the reaction (1) might be predominant for the mechanism of pyridyl radical formation.

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