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53. Michiya Itoh and Toshihiko Okamoto : Reductive Radical Formation of Hetero Aromatic N-Oxides.*1

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Pyridine 1-oxide gave the 4,4′-dipyridyl anion radical in 1,2-dimethoxyethane by reduction with the potassium metal *in vacuo*. The 3,5-lutidine, pyrazine and 3-nitropyridine anion radicals were also obtained from the parent N-oxides by the reduction, accompanied with the removal of oxygen atoms, while the 4-nitro- and 4-nitroso-pyridine 1-oxide anion radicals were obtained from the parent compounds without the deoxygenation.

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It has been reported that oxygen atoms of hetero aromatic N-oxides are removed with the phosphorous tri-halogenide[1] and triethyl phosphite,[2] and their reaction mechanisms have been discussed. On the course of the investigation of the electron spin resonance (ESR) and electronic spectra in the hetero aromatic negative or neutral radicals,[3,4] the present authors have attempted to prepare the anion radicals of various substituted pyridine or diazine 1-oxides leading to the conclusion that some hetero aromatic N-oxides give anion radicals, accompanied with the removal of oxygen atoms.

Results

When a 1,2-dimethoxyethane (abbreviated hereafter to DME) solution of pyridine 1-oxide was introduced to contact with pure sublimated potassium metal in a sealed glass vessel in high vacuum, as shown in Fig. 1, the DME solution became slightly red. The ESR spectrum of this DME solution was measured at room temperature, but any ESR spectrum was not observed. After this DME solution was kept in contact with potassium metal at room temperature for about 2 or 3 days, the solution gradually colored red brown. The ESR and electronic spectra were measured, with the results given in Fig. 2 and 3. On the other hand, the DME solution of pyridine was immediately colored red purple by contacting with potassium metal for only short period of time. The ESR spectrum of the red purple solution showed a strong hyperfine spectrum, which was identical with the spectrum as shown in Fig. 2. If this solution remained in contact with the potassium for about 15 minutes, the faded solution was obtained and it exhibited no ESR spectrum. Ward[5] reported that pyridine gives unstable 4,4′-dipyridyl anion radical by reduction with the alkali metal in DME, whose ESR spectrum was completely same as that in Fig. 2. Accordingly, it can be concluded that pyridine 1-oxide gave the 4,4′-dipyridyl anion radical through dimerization and deoxygenation reaction by introducing to contact with potassium metal *in vacuo*.

If a DME solution of 3,5-lutidine 1-oxide was allowed to remain in contact with potassium metal *in vacuo*, a slightly red solution was obtained. The ESR spectrum

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1) M. Hamana : Yakugaku Zasshi, **75**, 127 1955.
2) L. Garcis, M. Orchin : J. Chem. Soc., **1961**, 2254.
3) M. Itoh, T. Okamoto, S. Nagakura : Bull. Chem. Soc. Japan, **36**, 1665 (1963); M. Itoh, S. Nagakura : *Ibid.*, **38**, 825 (1965).
4) M. Itoh, S. Nagakura : *Ibid.*, **39**, 368 (1966).
5) R. L. Ward : J. Am. Chem. Soc., **83**, 3623 (1961).

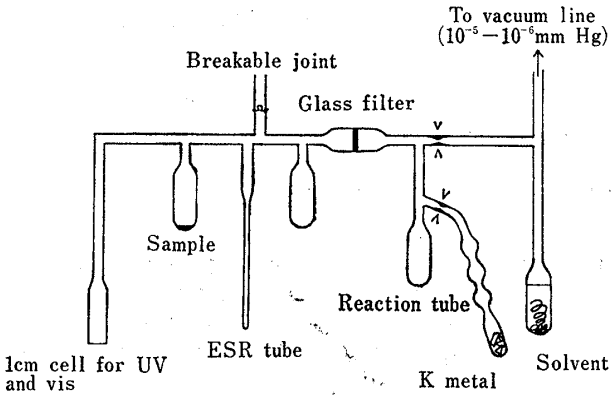


Fig. 1. The Reaction Vessel sealed in High Vacuum (glass).

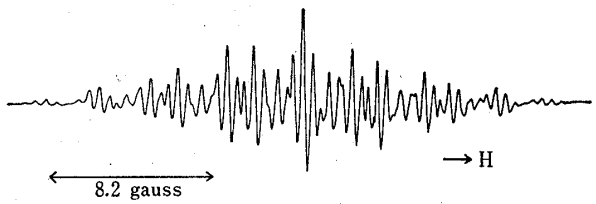


Fig. 2. The ESR Spectrum of 4,4′-Dipyridyl Anion Radical generated from Pyridine 1-Oxide

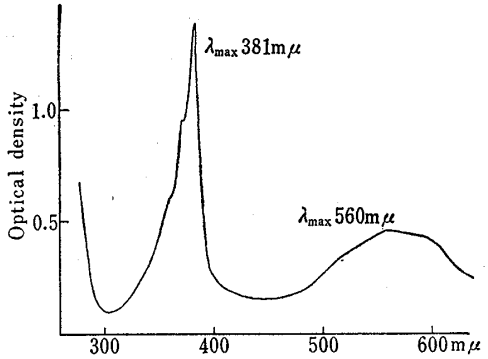


Fig. 3. The Electronic Absorption Spectrum of 4,4′-Dipyridyl Anion Radical generated from Pyridine 1-Oxide

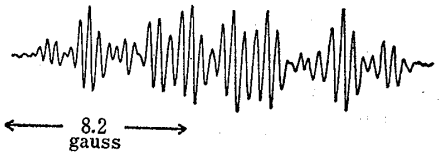


Fig. 4. The ESR Spectrum of 3,5-Lutidine Anion Radical generated from 3,5-Lutidine 1-Oxide

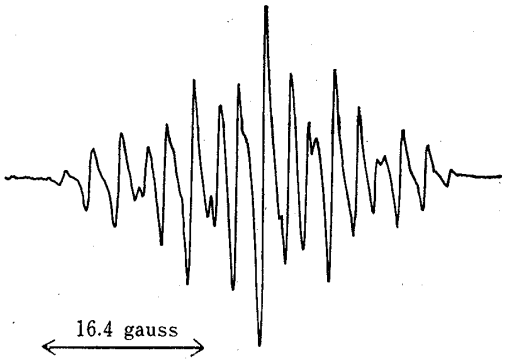
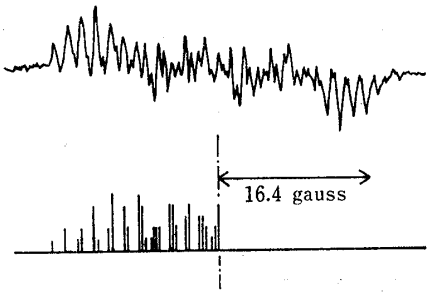


Fig. 5. The ESR Spectrum of Pyrazine Anion Radical generated from Pyrazine 1-Oxide



Fig, 6. The ESR Spectrum of 4-Nitroso-pyridine 1-Oxide Anion Radical and Its Reconstruction based on the Following Spliting Constants;
A_N (nitroso group)=7.80 gauss
A_N (ring nitrogen)=4.95 〃
A_H (2-position) =2.88 〃
A_H (3-position) =1.40 〃

was not observed in spite of repeated measurements. After this solution remained in contact with the metal for 2 or 3 days, this solution colored gradually red brown and showed strong ESR hyperfine spectrum as shown in Fig. 4. On the other hand, the ESR spectrum of the 3,5-lutidine anion radical[6] prepared from the 3,5-lutidine by the same procedures as those of its 1-oxide gave a quite same ESR spectrum as that shown in Fig. 4. From these results, the 3,5-lutidine anion radical was obtained from its 1-oxide, accompanied with the removal of oxygen atom. Pyrazine 1-oxide also gave the pyrazine anion radical[7] in DME through the similar course to that of the

6) N. M. Atherton, F. Gerson, J. N. Murrell: Mol. Phys., **5**, 500 (1962).
7) A. Carrington, J. dos Santos-Veiga: *Ibid.*, **5**, 21 (1962).

3,5-lutidine 1-oxide. In the previous paper, the ESR and electronic spectra of 3-nitropyridine anion radical were reported. 3-Nitropyridine 1-oxide also split off an oxygen atom to the 3-nitropyridine anion radical by reduction with the alkali metal.

The experimental results of 4-nitropyridine 1-oxide was already reported in the previous paper.[3] When a DME solution of 4-nitrosopyridine 1-oxide was kept in contact with the potassium metal *in vacuo*, the DME solution colored yellow from green in several hours. The ESR spectrum of this solution was measured, with the result given in Fig. 6. The splitting constants associated with nitrogen and hydrogen atoms were determined from the spectrum, as shown in Fig. 6. The spin densities on the 4-nitrosopyridine 1-oxide anion radical were also obtained from the splitting constants by the aid of the relationships between the splitting constants and the spin densities.*[3,3]

Discussion

The aromatic anion radicals generated with one electron reduction of the aromatic compounds by alkali metal are considered to be the ion pairs between the anion radicals and the counter cations, and these electronic interactions have been theoretically discussed.[8] In the nitrobenzene or some ketyl anion radicals generated by alkali metal reduction in DME or tetrahydrofuran, the metal cation may be situated near by the nitro or ketyl groups. The counter cation has been considered to be weakly attached to the most electronegative atoms or groups in the anion radicals of the other substituted aromatic compounds.

There is no doubt, as shown in the previous section, that pyrazine and lutidine 1-oxide give the anion radicals accompanied with the removal of the oxygen atoms from the parent N-oxides. The DME solution of pyridine 1-oxide was kept in contact with potassium metal during two days. After this period, the ESR spectrum of the 4,4′-dipyridyl anion radical was observed for about 1 or 2 days, though the 4,4′-dipyridyl anion radical was unstable. Ward reported that the 4,4′-dipyridyl anion radical was obtained from the pyridine in the degassed DME according to Eq.1.[5] He also suggested that potassium hydride could be formed from I. From our experimental

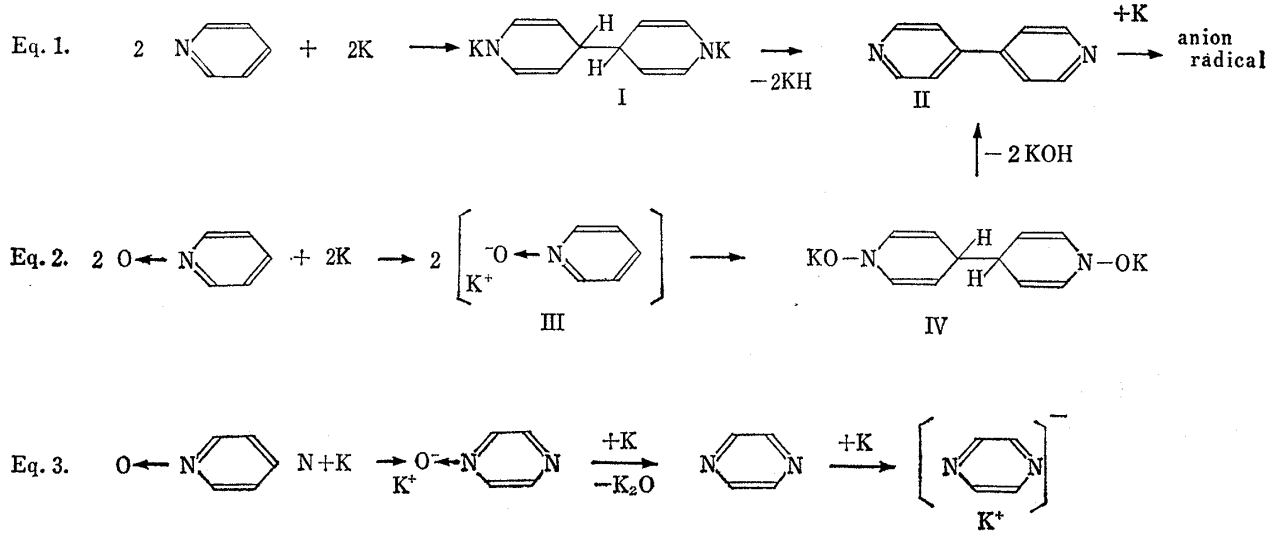


Chart 1.

*[3] The $A_N = 25.5\,\rho_N$ for the ring nitrogen atom, and the $A_N' = 40\,\rho_N'$ for the nitroso nitrogen atom, where A_N and A_N' are the splitting constants, and ρ_N and ρ_N' are the spin densities.

8) N. Hirota : J. Chem. Phys., **37**, 1884 (1962).

results, it can be inferred that the pyridine 1-oxide anion radical may be formed slowly in DME, but the concentration of this N-oxide anion radical (III) was not enough to be detected by ESR at room temperature. The further reaction proceeds according to Eq. 2. Subsequent dimerization of the pyridine 1-oxide anion radical and removal of potassium hydroxide also proceed slowly in aprotic solvent DME. It is not so clear whether the formation of the 4,4′-dipyridyl anion radical is performed through II from IV or directly from IV. Lutidine 1-oxide and pyrazine 1-oxide may be deoxygenated to subsequent formation of lutidine and pyrazine anion radicals, according to Eq. 3.

The present authors and Nagakura have reported the ESR and electronic structures of 3- and 4-nitropyridines and the 4-nitrosopyridine 1-oxide anion radicals.[3] The anion radical of 4-nitrosopyridine 1-oxide was also obtained without the removal of the oxygen atom of the 1-oxide group. The spin densities on the nitrogen and carbon

Table I. The Spin Densities of Nitrogen and Carbon Atoms of the 4-Nitropridine, 4-Nitropyridine 1-Oxide and 4-Nitrosopyridine 1-Oxide Anion Radicals

Position	4-NO_2-Py.	4-NO_2-Py. 1-O	4-NO-Py. 1-O
NO_2 or NO	0.218[a] (0.261)[b]	0.187[b]	0.195[c]
3-C	0.024 (0.033)	0.069	0.062
2-C	0.133 (0.052)	0.159	0.128
Ring N	0.101[d] (0.124)	0.181[d]	0.194

a) The spin densities on the nitrogen atoms of the nitro group, estimated by the following equation: $A_N=Q_N\cdot\rho_N$, $Q_N=40$ gauss.
b) The results obtained by the molecular orbital calculation, as shown in a previous paper.[8]
c) The spin density on the nitrogen atom in the nitroso group, estimated by the aid of $A'_N=Q'_N\cdot\rho'_N$, tentatively $Q'_N=40$ gauss.
d) The spin densities on the nitrogen atoms in the pyridine rings, using the relation: $A_N=25.5\,\rho_N$.

atoms of the several anion radicals are summarized in Table I. The theoretical and experimental results, as reported in the previous papers, indicated that the odd electron distribution on the nitro group and on the pyridine ring in the 4-nitropyridine anion radical amounts to 53 and 47 percent respectively, In the anion radicals of 4-nitro- or 4-nitroso-pyridine 1-oxides, the spin distribution decrease to 30~40 per cent on the nitro groups, and increase to 70~60 per cent on the pyridine 1-oxide rings. These results seem to be attributed to the increment of the electron affinity of the pyridine 1-oxide ring compared with that of the pyridine ring. The stability of the anion radical in the solvent depends on the delocalization of an odd electron in the radical molecules. In the anion radicals of the substituted benzene or pyridine, only the aromatics containing electron-attractive groups such as nitro or nitroso groups give the stable radicals by reduction with the alkali metal in the aprotic solvent.[9] In the anion radicals of the unsubstituted pyridine or diazine 1-oxides, the spin density on the hetero aromatic ring must amount to 100 per cent. Furthermore, considerable amount of odd electron distribution is expected to localize on the nitrogen and oxygen atoms in the hetero aromatic N-oxide negative radicals from the character of the molecular orbitals of these radicals.[3,10] As the results, the potassium cation tends to attach to the most electronegative nitrogen or oxygen atoms of N-oxide group, and splits the oxygen atom from the N-oxide group.

9) R. L. Ward: J. Am. Chem. Soc., **83**, 1296 (1963); J. Chem. Phys., **36**, 1405 (1962).
10) T. Kubota: J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kaggaku Zasshi), **80**, 578 (1959).

Experimental

Materials——Pyridine 1-oxide, 3,5-lutidine 1-oxide, pyrazine 1-oxide were prepared from the commercial materials by the methods given in literatures,[11] and were purified by repeating distillation or recrystallization before use. 3-Nitro[12] and 4-nitrosopyridine 1-oxides[13] were also obtained and purified by the methods presented in literatures. The melting points of these nitro or nitroso compounds were in good agreement with those in the literatures.

Reaction between Hetero Aromatic N-Oxide and Potassium Metal, and Measurements——The reduction of hetero aromatic N-oxides with potassium mental was performed at room temperature in DME (concetration : $10^{-2}\sim10^{-3}M$) *in vacuo*. The DME was refluxed and distilled on potassium metal. Furthermore, the solvent was distilled into the reaction vessel in which the solvent was kept in contact with the potassium metal in high vacuum. The potassium metal was purified by repeating sublimation *in vacuo*.

The reduction and measurements of the ESR and electronic absorption spectra were performed in high vacuum ($10^{-5}\sim10^{-6}$ mm. Hg) by using a vacuum line system. The ESR and electronic spectra were measured with a Hitachi X-band ESR spectrometer Model MPU-2B and a Cary recording spectrophotometer Model 14M, respectively.

11) E. Ochiai : J. Org. Chem., **18**, 534 (1953).
12) E. Ochiai, C. Kaneko : This Bulletin, **8**, 28 (1960).
13) E. Ochiai, H. Mitarashi : *Ibid.*, **11**, 1084 (1963).