Tautomerism of 1-Hydroxy-2-pyridone in the Excited Triplet State

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Summary Analysis of the dual phosphorescence of the title compound indicates the existence of a tautomeric equilibrium in the excited triplet state in methylcyclohexane at 77 K.

THE tautomeric equilibrium of 1-hydroxy-2-pyridone (HP) in the ground state has been well studied and shown to lie practically completely in favour of the keto-form by i.r. and u.v. spectrometric as well as photoelectron spectroscopic measurements,[1] whereas little attention has been paid to the tautomerism of HP and related hydroxamic acids in excited states. To investigate the triplet-state behaviour of HP, we have measured the phosphorescence spectra of HP, 1-ethoxy-2-pyridone (EP), and 2-ethoxypyridine 1-oxide (EPO) at liquid nitrogen temperature, and we now present the first spectroscopic evidence in support of the tautomerism of HP in the excited triplet state.

HP in an alcohol glass exhibits an excitation wavelength-independent phosphorescence spectrum at 464 nm whose behaviour is identical with that of EP, which has a structure corresponding to the keto-isomer of the tautomeric HP. On the other hand, the phosphorescence of EPO, whose structure corresponds to that of the enol isomer of HP, has a maximum at about 440 nm which is weak compared with those of HP and EP, thus providing no evidence for the existence of a tautomeric equilibrium in the triplet state.

In contrast with the behaviour in an alcohol glass, HP gives dual phosphorescence depending on excitation wavelength in methylcyclohexane at 77 K. Shorter-wavelength excitation increases the intensity of the short-wavelength emission relative to that of the long-wavelength emission, resulting in a shift of the emission maximum to shorter wavelengths. The Figure shows that the short- and long-wavelength phosphorescence spectra are very similar in both emission maximum and intensity to those of EPO and EP,

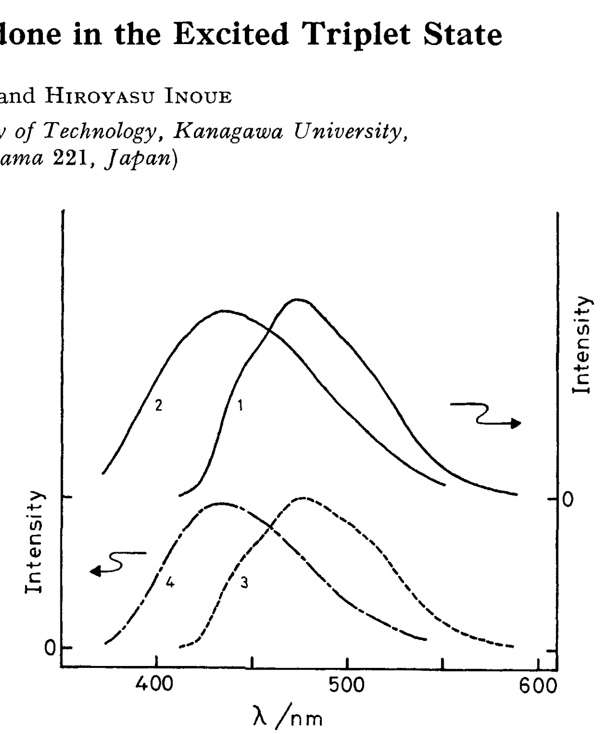

FIGURE. Phosphorescence spectra of HP (**1**,**2**), EP (**3**), and EPO (**4**) in methylcyclohexane at 77 K; excitation wavelengths: curves 1 and 3, 310 nm; curves 2 and 4, 279 nm; [HP], [EP], and [EPO] = 1·5—2·0 × 10^{-4} M.

respectively, suggesting the existence of a tautomeric equilibrium between the keto-isomer, 1-hydroxy-2-pyridone, and the enol isomer, 2-hydroxypyridine 1-oxide, in the triplet state. This possibility of tautomerization is further supported by the finding that the excitation spectra for the short- and long-wavelength phosphorescences nicely correspond with those for the EPO and EP phosphorescence, respectively. Thus, we conclude that tautomerization to the enol isomer form occurs to an appreciable extent in the triplet state. The failure to observe the enol isomer spectrophotometrically in the ground state clearly shows that the ground-state enol isomer is thermodynamically unstable and reverts to the more stable keto isomer.

Although we have no definitive evidence concerning the mechanism of tautomerization, the observation that HP is strongly hydrogen bonding intramolecularly as a monomer in inert solvents[1b] suggests that an intramolecular process is very likely. The facts that polar solvents weaken hydrogen bonds, and that both intra- and inter-molecular proton transfers are entropically unfavourable because the carbonyl oxygen atom in the pyridone skeleton is readily solvated by hydrogen bonds in protic solvents[2] might be responsible for the failure to observe the tautomerism of HP in a polar and proton-donating matrix.

(*Received*, 29*th June* 1981; *Com.* 757.)

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