

INTRAMOLECULAR PROTON TRANSFER REACTION OF *ORTHO*-NITROBENZYL COMPOUNDS: TIME-RESOLVED RAMAN AND ABSORPTION STUDY

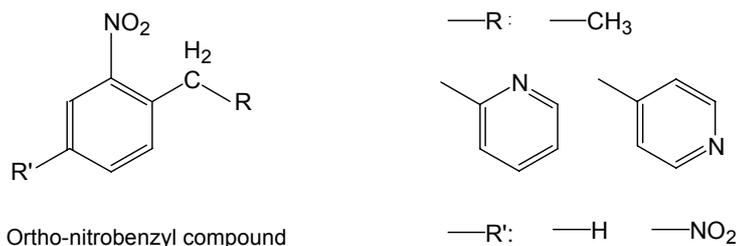
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Abstract: This contribution reports on time-resolved Raman and absorption spectroscopies of photo-induced intramolecular proton transfer reaction of *ortho*-nitrobenzyl compounds. A reaction scheme is presented for each of these compounds based on experimental results.

Ortho-nitrobenzyl compounds (shown below) are known to undergo reversible intramolecular proton transfer reaction from the ethylene group to the *ortho*-nitro group when irradiated with UV light. This investigation was undertaken with the purpose of obtaining information on the proton transfer reaction mechanism of these compounds having multiple proton-accepting sites (nitro group, 2-pyridyl and 4-pyridyl groups) using nanosecond time-resolved Raman and absorption spectroscopies.



As a representative of these compounds the photoreaction of 2-(2'-nitrobenzyl)pyridine (2-NBP) is discussed here. 2-NBP exhibited a strong absorption band at 433 nm, a very weak band at 571 nm and a shoulder at 366 nm in methanol at 100 ns delay time after irradiation with 308 nm light. At 5 μ s the band at 433 nm decreased in intensity with time with concomitant increases in intensity of the band at 366 and 571 nm. At 40 μ s the 433 nm band disappeared almost completely while the bands at 366 and 571 nm further increased in intensity as shown in Fig.1 (a). These spectral changes were not observed in CCl₄ solutions where the intensity decrease of the 450 nm band (corresponding band of the 433 nm band in methanol) with time was the only spectral change. The isosbestic points at around 370 and 500 nm indicated that two kinds of transient species, one exhibiting a band at 433 nm and the other, generated from the 433 nm species and exhibiting the bands at 366 and 571 nm, were involved in the photoreaction of this compound in the 100 ns to 40 μ s time domain.

The band at 433 nm can be assigned to the aci-nitro acid generated in terms of the proton transfer from the ethylene group to an oxygen atom of the *ortho*-nitro group. The bands at 366 and 571 nm are attributed to the *ortho* N-H quinoid isomer generated by accepting hydrogen by the nitrogen atom of the 2-pyridyl group. Since the absorption band of the aci-nitro anion was observed at 485 nm in methanol when NaOH was added to the solutions as shown in Fig. 1(b), it appeared that the aci-nitro anion was not produced in the photoreaction of this compound in neutral methanol and the *ortho* N-H quinoid was produced directly from the aci-nitro acid. However, since the *ortho* N-H quinoid was not detected in non-polar CCl₄ solutions, the aci-nitro anion should be generated by dissociation of the aci-nitro acid in polar methanol solutions with the lifetime being too short to be

detected in this time domain.

Time-resolved resonance Raman spectra of 2-NBP in methanol measured with 308 nm pumping and 390 nm probing showed a strong band at 1511 cm^{-1} which is considered to be characteristic to the ortho aci-nitro acid structure. In the photoreaction of 2-nitroethylbenzene (2-NEB), where only the aci-nitro acid was generated in neutral methanol, a strong Raman band was observed at 1516 cm^{-1} . These bands characteristic to the aci-nitro acid structure can be assigned to the C=C symmetric stretch of the quinoid ring based on DFT normal coordinate calculations. The photoreaction of 2-NBP can be expressed schematically as shown in Fig. 3

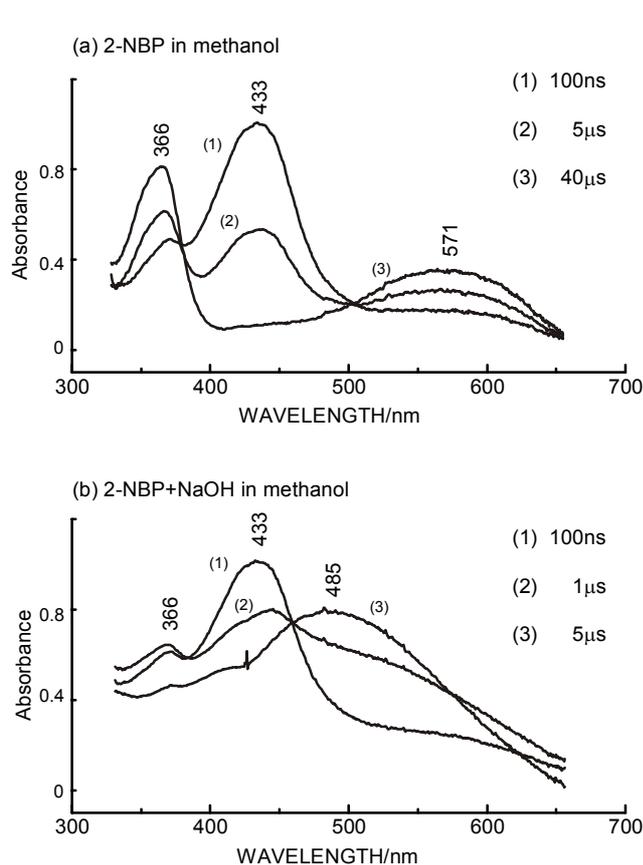


Fig. 1 Time-resolved absorption spectra of 2-NBP
Pump wavelength: 308nm

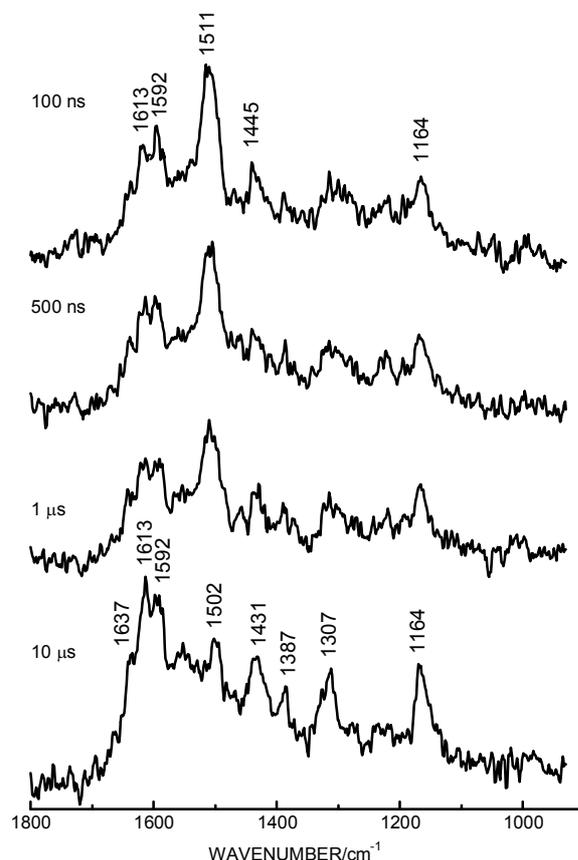


Fig. 2 Time-resolved resonance Raman spectra of 2-NBP in methanol. Pump wavelength: 308. Probe wavelength: 390nm

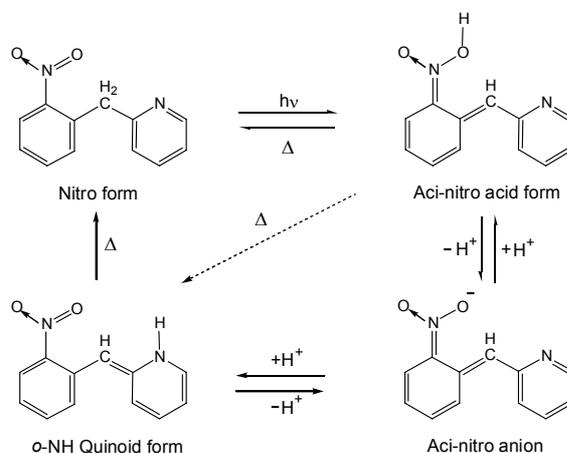


Fig. 3 Photoreaction scheme of 2-(2'-Nitrobenzyl)pyridine (2-NBP)