

# PHOTOINDUCED INTRAMOLECULAR HYDROGEN TRANSFER REACTION OF *ORTHO* NITROBENZYL COMPOUNDS

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Time-resolved resonance Raman and absorption spectra have revealed that the photoinduced intramolecular hydrogen transfer reaction of *ortho* nitrobenzyl compounds is initiated by the abstraction of methylene hydrogen by the *ortho* nitro group to generate the *ortho* aci-nitro acid isomer. In polar solvents the *ortho* aci-nitro acid is dissociated into the aci-nitro anion and a proton, and the proton is captured by other hydrogen accepting sites, such as 2-pyridyl, 4-pyridyl and 4-nitro groups to generate the *ortho* N—H quinoid, *para* N—H quinoid and *para* aci-nitro acid isomers, respectively. For 2-nitroethylbenzene and 2- and 4-(2'-nitrobenzyl)pyridines the structure of the aci-nitro anion is very similar to that of their respective *ortho* aci-nitro acid, while for 2,4-dinitroethylbenzene the structure of the aci-nitro anion quite resembles that of the *para* aci-nitro acid.

*Keywords:* Ortho nitrobenzyl compounds; photoinduced hydrogen transfer; time-resolved Raman; time-resolved absorption

## INTRODUCTION

Benzyl derivatives having a nitro group at the *ortho* position are known to undergo photoinduced reversible intramolecular transfer of methylene hydrogen of the benzyl group. However, the detailed mechanism of this hydrogen transfer reaction is not well understood. This investigation was carried out with the purpose of obtaining

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detailed information on the hydrogen transfer mechanism of *ortho* nitrobenzyl compounds having multiple possible hydrogen accepting sites using time-resolved Raman spectroscopy and laser flash photolysis with the help of *ab initio* molecular orbital calculations.

## EXPERIMENTAL

2-Nitroethylbenzene was purchased from Tokyo Kasei Kogyo Co. Ltd. 2,4-dinitroethylbenzene was synthesized by nitration of 2-nitroethylbenzene. 2-(2'-Nitrobenzyl)pyridine and 4-(2'-nitrobenzyl)pyridine were synthesized by nitration of commercially available 2-benzylpyridine and 4-benzylpyridine (Kanto Chemical Co. Inc.) to generate 2-(2',4'-dinitrobenzyl)pyridine and 4-(2',4'-dinitrobenzyl)pyridine, respectively, followed by elimination of the 4-nitro group through the diazonium salt.

## RESULTS AND DISCUSSION

### 2-Nitroethylbenzene (NEB)

The transient absorption spectrum of NEB in methanol measured at 100 ns after the pumping with 308 nm light exhibited a band at 395 nm which decreased in intensity with time, but was not affected by the presence of oxygen. This band is assignable to the *ortho* aci-nitro acid isomer generated by hydrogen transfer from the methylene group to the *ortho* nitro group. With addition of NaOH in methanol solutions (about 1/20 of NEB in molar concentration) the 395 nm band exhibited a shifting to 410 nm with time. The band at 410 nm can be attributed to the aci-nitro anion produced by dissociation of the *ortho* aci-nitro acid. Since the peak shift on the dissociation is small, the absorption of a small amount of the aci-nitro anion may well be hidden under the strong 395 nm band, and therefore, the possibility of the generation of a small amount of the aci-nitro anion in the hydrogen transfer reaction of NEB in neutral methanol solutions may not wholly be excluded.

The transient resonance Raman spectrum of NEB measured with 423 nm light at 100 ns after the 308 nm pumping in methanol was

compared with that in  $\text{CCl}_4$  (Fig. 1). We found that the weak band at  $1282\text{ cm}^{-1}$  observed in methanol solutions was missing in the spectrum of  $\text{CCl}_4$  solutions. Since the dissociation of the aci-nitro acid is expected to occur only in polar solvents, and NEB in alkaline methanol solutions exhibited a strong Raman band at  $1288\text{ cm}^{-1}$ , the  $1282\text{ cm}^{-1}$  band observed in methanol solutions indicates that a small amount of the aci-nitro anion is produced in neutral methanol solutions.

It was observed that the spectrum of the aci-nitro anion is very similar to that of the aci-nitro acid. This implies that the structures of

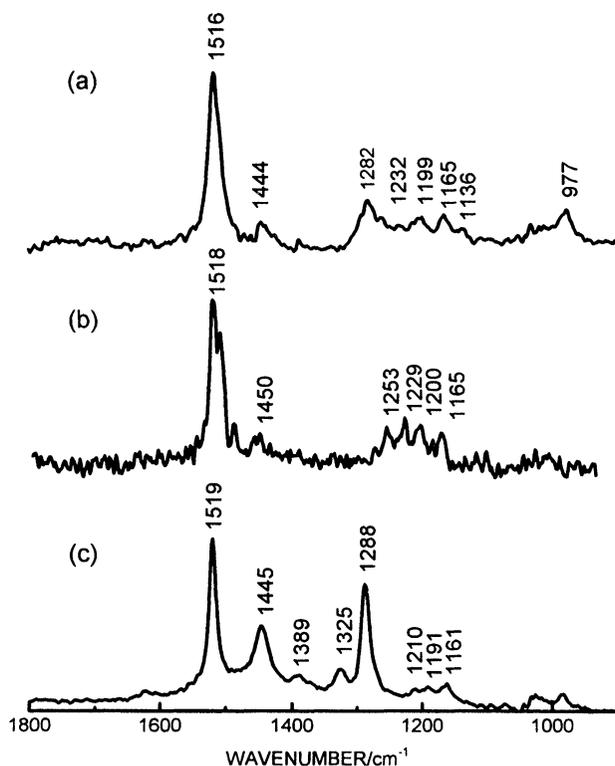


FIGURE 1 Transient resonance Raman spectra of NEB in different solvents (concentration,  $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ ) probed with 423 nm light: (a) methanol solution observed at 100 ns; (b)  $\text{CCl}_4$  solution observed at 100 ns; (c) basic methanol solution observed at 10  $\mu\text{s}$  (concentration of NaOH,  $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ ). Pump wavelength, 308 nm.

the both transients quite resemble each other. Also, the strong Raman band at about  $1515\text{ cm}^{-1}$  observed in the both transients may be considered to be the characteristic band of the *ortho* quinoidal structure of the aci-nitro acid and its anion. *Ab initio* molecular orbital calculations of the optimized geometries and normal frequencies using the DFT(density functional theory)/B3LYP method nicely supported the above conclusions and showed that the  $1515\text{ cm}^{-1}$  band is assigned to the symmetric stretch of the C=C bonds in the *ortho* quinoidal ring.

### **2-(2'-Nitrobenzyl)pyridine (2-NBP) and 4-(2'-nitrobenzyl)pyridine (4-NBP)**

Since the hydrogen transfer reaction of 2-NBP is similar to that of 4-NBP, only 4-NBP is discussed here. 4-NBP in methanol exhibited an absorption band at 423 nm at 100 ns after the 308 nm pumping. At  $2\ \mu\text{s}$  a shoulder appeared at ca. 390 nm and at  $10\ \mu\text{s}$  the 423 nm band with the 390 nm shoulder disappeared completely while new bands appeared at 379 and 544 nm. These spectral changes were not observed in  $\text{CCl}_4$  solutions. The band at 423 nm can be assigned to the aci-nitro acid isomer. The shoulder at about 390 nm is attributed to the aci-nitro anion, because in basic methanol solutions a broad band assignable to the aci-nitro anion was observed at 392 nm. The bands at 379 and 544 nm are assigned to the *ortho* N-H quinoid isomer generated from the aci-nitro anion by accepting a proton at the nitrogen atom of the 4-pyridyl group.

The transient resonance Raman spectrum of 4-NBP in methanol measured with 423 nm light at 100 ns showed a strong band at  $1512\text{ cm}^{-1}$ , which is characteristic to the *ortho* aci-nitro acid structure, and a band at  $1292\text{ cm}^{-1}$  with a shoulder at about  $1280\text{ cm}^{-1}$ . At  $100\ \mu\text{s}$  these bands disappeared and bands are observed at 1655, 1592 and  $1541\text{ cm}^{-1}$  which are attributable to the *para* N-H quinoid isomer. The  $1280\text{ cm}^{-1}$  shoulder may arise from the aci-nitro anion, because in basic methanol solutions the aci-nitro anion exhibited a strong bands at 1519 and  $1277\text{ cm}^{-1}$ . The transient resonance Raman spectrum measured with 390 nm light at 100 ns was almost the same as the spectrum of the aci-nitro anion.

**2,4-Dinitroethylbenzene (DNEB)**

On irradiation with 308 nm light DNEB in methanol exhibited two absorption peaks at ca. 335 and 465 nm at 100 ns after the pumping. These bands decreased in intensity with time and at 10  $\mu$ s a strong band appeared at 343 nm. In basic methanol solutions two absorption peaks were observed at 363 and 393 nm. The bands at ca. 335 and 465 nm are assignable to the *ortho* aci-nitro acid isomer. It was

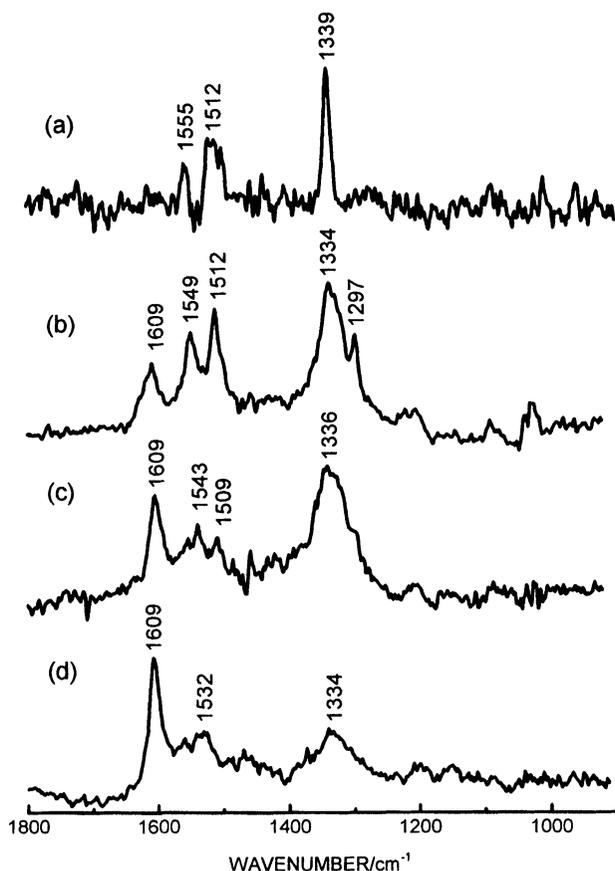


FIGURE 2 Transient resonance Raman spectra of DNEB in different solvents (concentration,  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>) probed with 456 nm light: (a) CCl<sub>4</sub> solution observed at 100 ns; (b) methanol solution observed at 100 ns; (c) methanol solution observed at 2  $\mu$ s; (d) basic methanol solution observed at 100  $\mu$ s (concentration of NaOH,  $1.4 \times 10^{-4}$  mol dm<sup>-3</sup>). Pump wavelength, 308 nm.

observed that in acidic methanol solutions the generation of the transient exhibiting the 343 nm band was markedly accelerated. The band at 343 nm can be attributed to the *para* aci-nitro acid isomer. The shortening of the rise time of the 343 nm band in acidic methanol solutions may be explained as due to the protonation of the 4-nitro group with the concomitant deprotonation of the *ortho* aci-nitro acid group to generate the *para* aci-nitro acid isomer. It is not clear from the absorption spectra whether or not the aci-nitro anion is produced in neutral methanol solutions as the precursor of the *para* aci-nitro acid.

The transient resonance Raman spectrum of DNEB probed with 456 nm light at 100 ns in methanol exhibited bands at 1609, 1549, 1512 and 1334  $\text{cm}^{-1}$  (Fig. 2). The 1609  $\text{cm}^{-1}$  band, however, was missing in the spectrum of  $\text{CCl}_4$  solutions. The band at 1549, 1512 and 1334  $\text{cm}^{-1}$  are attributable to the *ortho* aci-nitro acid isomer. The band at 1609  $\text{cm}^{-1}$  is considered to arise from the aci-nitro anion, because basic methanol solutions exhibit a strong Raman band at 1609  $\text{cm}^{-1}$  which is attributable to the aci-nitro anion. At 100  $\mu\text{s}$  the band at 1609 became stronger and the bands at 1549 and 1512  $\text{cm}^{-1}$  disappeared and new bands appeared at 1543 and 1509  $\text{cm}^{-1}$ . These bands are assigned to the *para* aci-nitro acid isomer. The spectral change with time indicates that the *para* aci-nitro acid was produced by the protonation of the aci-nitro anion which was generated by the dissociation of the *ortho* aci-nitro acid. On the basis of the similarity of the spectra it is concluded that the structure of the aci-nitro anion is very similar to that of the *para* aci-nitro acid.