

FORMATION OF 1-NITRO-2-HYDROXYPYRENE FROM 1-NITROPYRENE
BY PHOTOLYSIS

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1-Nitropyrene was converted by photolysis to a new compound, deep red needles, which was identified to be 1-nitro-2-hydroxypyrene.

Strongly carcinogenic and mutagenic 1-nitropyrene(I) has already been determined in environmental samples, for example diesel exhaust and airborne particulate matter.¹⁻⁵⁾ It was confirmed by several investigators that I is formed from pyrene by nitration with NO₂.⁶⁻⁸⁾ Some analytical techniques have been developed for determination of I.^{5,9-11)} A fate of I in environment is very interesting since I is fairly unstable and reactive against heat or light. It is very important what occurs by thermolysis or photolysis and whether the reaction products are carcinogenic. Recently thermolysis product was tentatively identified to be 1-aminopyrene.¹²⁾ However, photolysis product remains undetermined. This paper deals with the determination of photoreaction product of I.

I (0.490 g), prepared according to the literature,¹³⁾ was dissolved in acetonitrile (1000 mL) and the solution was irradiated with a 400W high-pressure mercury lamp, which emits the light of wavelengths over 250 nm, under the conditions exposed with air and stirring for 5 h. Reaction products were checked with thin-layer silica gel chromatography, where the solvent used was carbon tetrachloride. Two spots were observed mainly. The spot with R_f value of 0.42 coincided with reference spot of I. A new compound(II) with R_f value of 0.53 were separated from I by column chromatography using silica gel (Merck, 140 g), where carbon tetrachloride was used as an elution solvent. Recovered amounts of I was 0.282 g. Deep red needles of II (0.167 g), which were easily sublimed, were obtained after recrystallization from benzene: mp 227-229°C; IR (KBr disk) 3060-3050, 1600, 1534, 1470, 1425, 1408, 1325, 1287, 1270, 1200, 1150, 1138, 1110, 1063, 984, 950, 872, 840, 825, 778, 762, 680, 625 cm⁻¹; UV (THF) λ_{max} (ε) 219(218000), 257.5(190000), 266(301000), 309.5(388000), 349(198000), 474nm(30700). Anal. Found: C, 72.86; H, 3.48; N, 5.20. Mass spectrum¹⁴⁾ showed that molecular weight of II was 263, the number of carbon atom in a molecule was 16 from isotope peak ratio, and nitro group was present. The 400-MHz ¹H NMR spectrum, shown in Fig. 1, gave the information that only aromatic protons and hydroxyl proton existed. The structure of II was determined to be 1-nitro-2-hydroxypyrene from these data. Determination of II in airborne particulate matter or soots are now in progress.

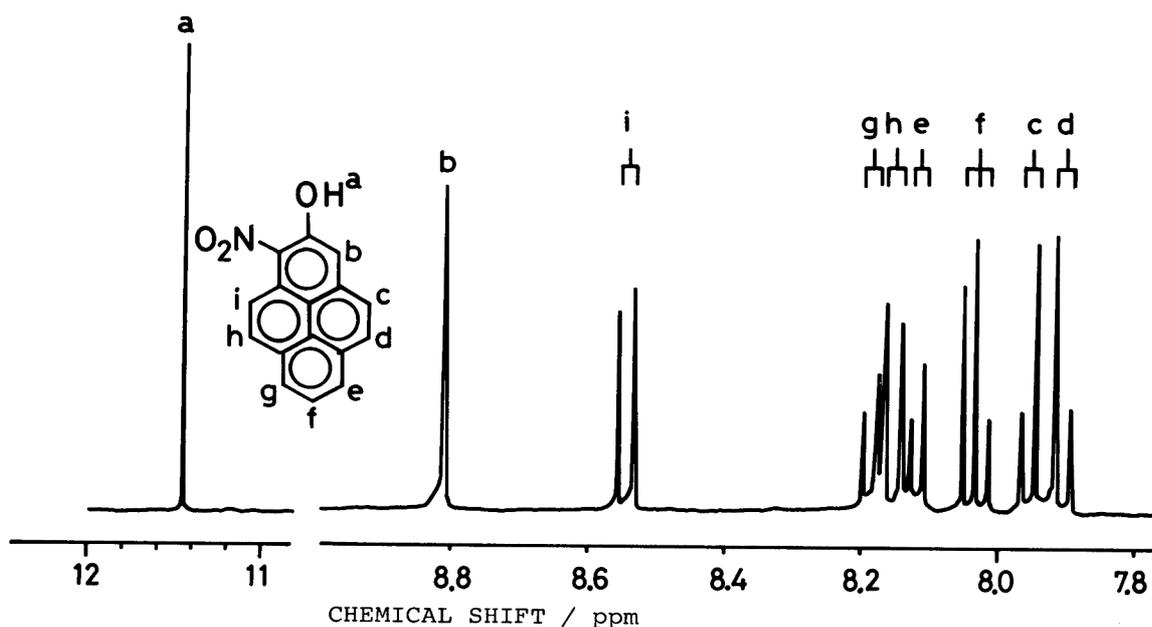


Figure 1 400-MHz ^1H NMR spectrum of II in THF-d_8

We thank Masayuki Kunugi for measuring 400-MHz ^1H NMR spectra.

References

- 1) E.T.Wei, Y.Y.Wang, S.M.Rappaport, *J.Air Pollut. Contr. Ass.*, **30**, 267(1980).
- 2) K.Morita, K.Fukamachi, H.Tokiwa, *Bunseki Kagaku*, **31**, 255(1982).
- 3) X.B.Xu, J.Nachtman, Z.L.Jin, E.T.Wei, S.M.Rappaport, *Anal.Chim.Acta*, **136**, 163 (1982).
- 4) D.Schuetzle, F.S.-C.Lee, T.J.Prater, *Int.J. Environ. Anal. Chem.*, **9**, 93(1981).
- 5) D.L.Newton, M.D.Erickson, K.B.Tomer, E.D.Pellizzari, P.Gentry, R.B.Zweidinger, *Environ.Sci.Technol.*, **16**, 206(1982).
- 6) J.N.Pitts, Jr., K.A.V.Cauwenberghe, D.Grosjean, J.P.Schmit, D.R.Fitz, W.L.Belser, Jr., G.B.Knudson, P.M.Hynds, *Science*, **202**, 515(1978).
- 7) J.D.Butler, P.Crossley, *Atmos. Environ.*, **15**, 91(1981).
- 8) J.A.Yergey, T.H.Risby, S.S.Lestz, *Anal.Chem.*, **54**, 354(1982).
- 9) D.Schuetzle, T.L.Riley, T.J.Prater, T.M.Harvey, D.F.Hunt, *Anal.Chem.*, **54**, 265 (1982).
- 10) S.M.Rappaport, Z.L.Jin, X.B.Xu, *J.Chromatogr.*, **240**, 145(1982).
- 11) T.Ramdahl, K.Urdal, *Anal.Chem.*, **54**, 2256(1982).
- 12) J.A.Sweetman, F.W.Karasek, *J.Chromatogr.*, **247**, 245(1982).
- 13) H.Vollmann, H.Becker, M.Corell, H.Streeck, *Justus Liebigs Ann.Chem.*, **531**, 1(1937).
- 14) Mass spectral data; m/z (rel. int.) 264(18), 263(100), 247(5), 246(20), 233(8), 218(5), 217(24), 216(42), 205(5), 190(5), 189(34), 188(73), 187(40), 186(5), 132(16), 108(12), 95(18), 94(30), 88(7), 87(7), 63(5), 30(7).

(Received January 17, 1983)