

Short Communication

Electron transfer from chloride ion to the triplet state of 5-nitroindole

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(Received July 6, 1984)

In a previous report from this laboratory we demonstrated the electron transfer to the triplet state of some aromatic nitro compounds from the chloride ion, when present as HCl [1, 2]. As an extension of our interest in these molecules we have undertaken a flash photolysis study of 5-nitroindole (5-NI) in 50% (isopropyl alcohol)-water containing HCl and H₂SO₄. The flash excitation of vacuum-degassed 6.6×10^{-5} M 5-NI in 50% (isopropyl alcohol)-water, 6 N in HCl, gives rise to a transient in the region 400 - 460 nm with a lifetime of 18 ms. The appearance of this transient depends, as is seen in Fig. 1, on the concentration of HCl and does not appear to any significant extent in 6 N H₂SO₄. No transient signal was detected in 4 N H₂SO₄ and little photochemistry was observed in 4 and 6 N H₂SO₄ solutions. We were unable to make measurements below 400 nm because of significant ground state absorption below this wavelength. By comparison with the known spectrum of the protonated nitrobenzene anion [1], it is reasonable to attribute the origin of the transient in 6 N HCl to the protonated anion radical of 5-NI with the electron transfer from the chloride ion to the π, π^* triplet of 5-NI as the primary process, *i.e.*

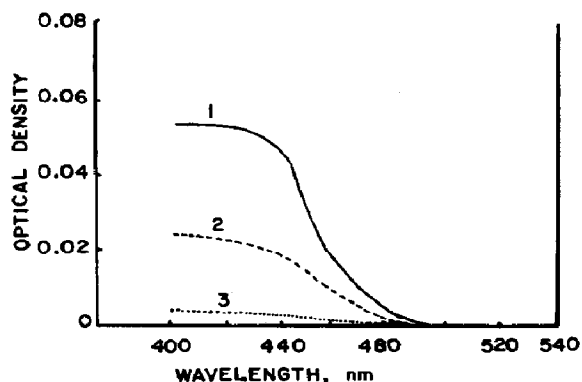
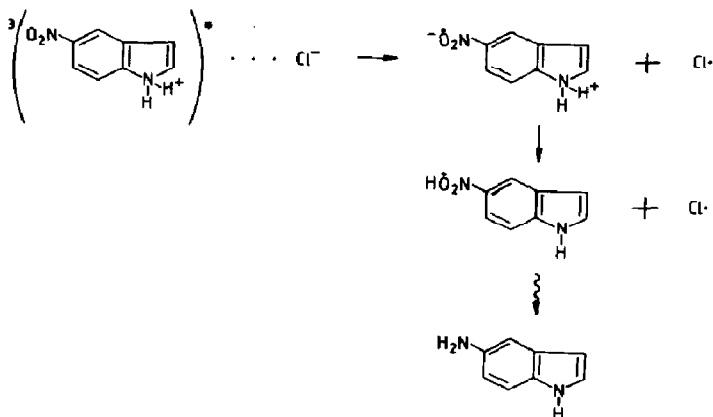


Fig. 1. Flash photolysis transient ($\tau = 18$ ms) observed for degassed 6.6×10^{-5} M 5-NI in 50% (isopropyl alcohol)-water with 6 N HCl (curve 1), 2 N HCl (curve 2) and 6 N H₂SO₄ (curve 3).



Further reduction leads to the aminoindole. The UV absorption spectrum of degassed 6.6×10^{-5} M 5-NI in 50% (isopropyl alcohol)–water with 4 N HCl, before and after flashing, is shown in Fig. 2, where it is evident that two absorption peaks of 5-NI at 330 and 267 nm decrease while the new bands appearing at 223 and 287 nm provide evidence for the aminoindole. The UV spectrum of a sublimed sample of the latter in 50% (isopropyl alcohol)–water with 2 N HCl shows peaks at 285 and 220 nm with the latter having a higher intensity. Noteworthy is the presence of isosbestic points at 237, 278 and 305 nm, which suggest that the photochemical conversion of the nitro

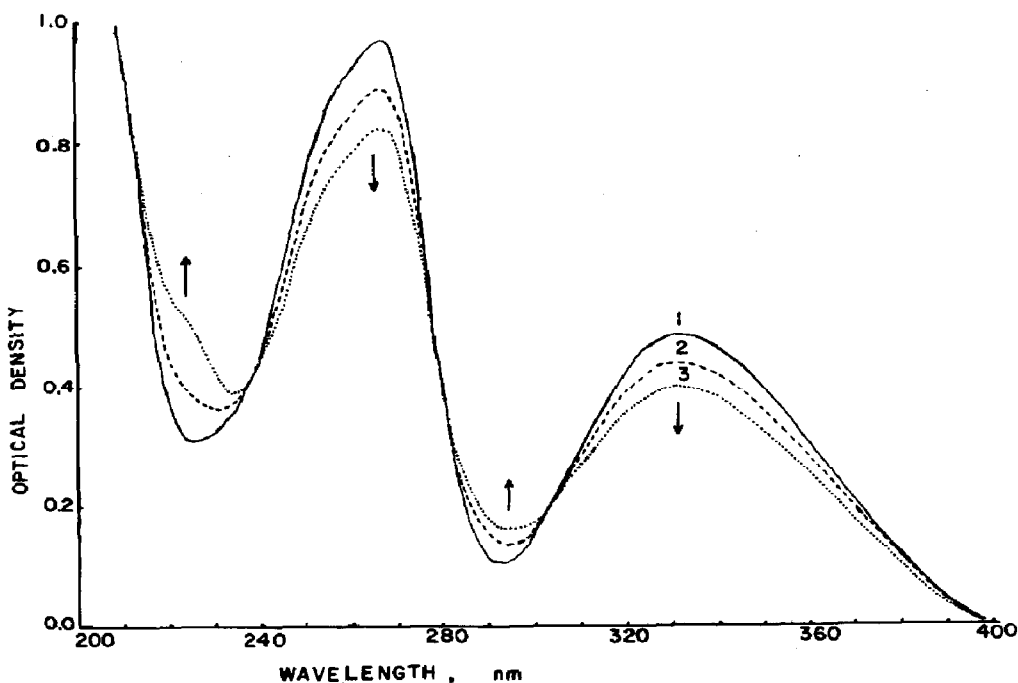


Fig. 2. UV absorption spectrum of 5.5×10^{-5} M 5-NI in 50% (isopropyl alcohol)–water with 4 N HCl: curve 1 degassed solution before flashing; curve 2 after 13 flashes; curve 3 after 37 flashes.

compound in the presence of alcohol and HCl is a relatively simple photochemical process.

In conclusion, the above results provide additional evidence for the electron transfer from the chloride ion, when present as HCl, to the excited triplet state of aromatic nitro compounds. Since this process occurs with molecules possessing n, π^* or π, π^* triplet levels, it appears that the only important factor for its observation is the energy of its lowest triplet state.

1 A. Cu and A. C. Testa, *J. Am. Chem. Soc.*, 96 (1974) 1963.

2 A. Cu and A. C. Testa, *J. Photochem.*, 6 (1977) 277.