Reversible Hydrogen Photoabstraction by Nitroaromatic Compounds. A Chemically Induced Nuclear Polarization Study

By **Karol A. Muszkat** * and **Meir Weinstein**,* Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

Proton nuclear polarization is observed in the photoreaction of aromatic nitro-compounds with 2,6-di-t-butylphenols. The polarization is due to a reversible abstraction of the phenol hydroxy-hydrogen by the excited triplet nitro-compound. The occurrence of polarization depends on the triplet energy of the nitro-compound and on the O–H bond dissociation energy of the phenol. Observation of polarization forms the basis for the estimation of the O–H bond dissociation energy of $ArNO_2H\cdot$ radicals.

WE have recently reported a CIDNP [1] study of reversible hydrogen transfer between triplet excited xanthen dyes

$$^3D + ArOH \longrightarrow ArO\cdot + DH\cdot \tag{1}$$

$$ArO\cdot + DH\cdot \longrightarrow Ar^*OH + D \tag{2}$$

(^3D) and hydroxy-groups of various phenols [steps (1) and (2)].[2,†] In this paper we report a related general reaction in which triplet excited nitroaromatic compounds ($^3Ar^1NO_2$) abstract hydrogen reversibly from 2,6-di-t-butylphenol and from the 4-methyl derivative (BHT).

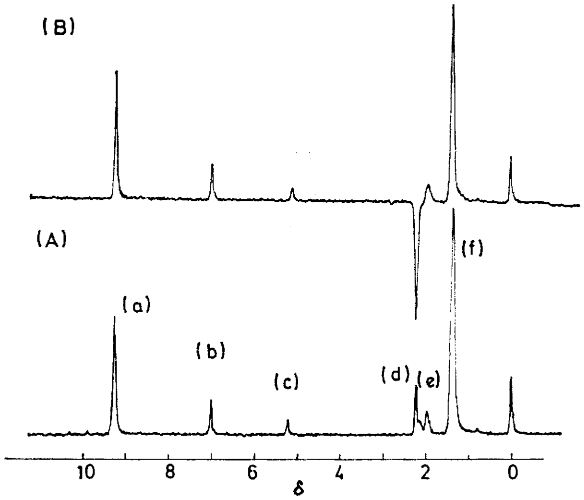


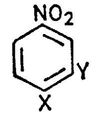
FIGURE 1 90 MHz ^1H N.m.r. spectra of CD_3CN solution containing both 1,3,5-trinitrobenzene and BHT: (A) without u.v. irradiation; (B) during u.v. irradiation. (a) 1,3,5-Trinitrobenzene ring protons; (b)—(d) and (f) BHT protons (ring, OH, 4-methyl, and t-butyl respectively); (e) solvent

U.v. irradiation inside the n.m.r. probe, of CD_3CN solutions of a wide range of aromatic nitro-compounds in the presence of BHT results in polarization (emission) of the 4-methyl protons of BHT. Typical results, obtained on irradiating 1,3,5-trinitrobenzene–BHT solutions are shown in Figure 1. This effect and the absence of other photoproducts even after relatively long periods of irradiation suggest that the overall process taking place is a reversible hydrogen transfer, as in steps (3) and (4).

$$^3Ar^1NO_2 + Ar^2OH \longrightarrow {}^3Ar^1NO_2H\cdot + Ar^2O\cdot \tag{3}$$

$$Ar^1NO_2H\cdot + Ar^2O\cdot \longrightarrow Ar^1NO_2 + Ar^{2*}OH \tag{4}$$

The photo-CIDNP effect in BHT was observed in the presence of the following nitro-compounds: (a) nitrobenzene and derivatives (Y = H, X = H, Cl, Br, I, CH_3, C_6H_5, CH_2CO_2H, CH_3O, C_2H_5O, and CN); (b) dinitrobenzenes and derivatives (Y = H, X = NO_2; Y = NO_2, X = H, CH_3, CH_2CO_2H,F,Cl,Br); and (c) 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, picric acid, and 1,5-dinitronaphthalene.



The polarization of the 4-methyl protons in BHT is due to nuclear spin level selection [3] during T_0–S crossing in the initially spin-correlated radical pair $\overline{^3Ar^1NO_2H\cdot + Ar^2O\cdot}$ (RP1). Kaptein's rules for deriving Γ_{NE}, the sign of the effect observed are applied here as follows: [3] Ar^*OH is formed by recombination in RP1. RP1 is initially in a triplet electronic spin state since $^3Ar^1NO_2$ is known to be formed by intersystem crossing [4] in singlet excited Ar^1NO_2.[‡] Both labels μ and ε are therefore positive. The 4-methyl protons hyperfine coupling constant A_i in $ArO\cdot$ is also positive.[5] Thus the observed *negative* sign of the net effect Γ_{NE} ($\Gamma_{NE} = \mu\varepsilon\Delta g A_i = -$) [3] requires that Δg, the sign of the difference

---

[†] Asterisk denotes nuclear polarization.

[‡] Phosphorescence lifetimes at 77 K are short as a rule, but strong phosphorescence is observed in some cases, *e.g.* 4-nitrobiphenyl. Quenching of excited triplet states by phenols is much more efficient than of excited singlets (*e.g.* in xanthen dyes, L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.*, 1961, **34**, 1411).

[1] For recent reviews see A. R. Lepley and G. L. Closs, ' Chemically Induced Magnetic Polarization,' Wiley, New York, 1973.

[2] K. A. Muszkat and M. Weinstein, *J.C.S. Chem. Comm.*, 1975, 143.

[3] R. Kaptein, *J.C.S. Chem. Comm.*, 1971, 732; *J. Amer. Chem. Soc.*, 1972, **94**, 6251.

[4] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100; S. P. McGlynn, T. Azumi, and M. Kinoshita, ' Molecular Spectroscopy of the Triplet State,' Prentice-Hall, Englewood Cliffs, 1969, p. 251.

[5] P. B. Ayscough, ' Electron Spin Resonance in Chemistry,' Methuen, London, 1967, ch. 8.

in the g factors, $g(Ar^2O\cdot) - g(Ar^1NO_2H\cdot)$ be negative also. The limited relevant experimental data available indeed show this to be true. Thus for 2,4,6-tri-t-butylphenoxyl radical, $g = 2.004\,47 \pm 0.000\,07$ [6b] and for the *p*-nitrobenzene anion radical, $g = 2.005\,1$.[6b] For the pair 4-methyl-2,6-di-t-butylphenoxyl–nitrobenzene anion radical Δg was determined directly in the present work (see Experimental section). The value obtained for $g(Ar^2O\cdot) - g(Ar^1NO_2^{-}\cdot)$ is $-0.001\,2$.§

A possible escape process of $Ar^2O\cdot$ from RP1, $Ar^2OH + Ar^*O\cdot \longrightarrow Ar^2O\cdot + Ar^*OH$ is very slow (k 300 l mol^{-1} s^{-1})[8] and considering the low O–H bond energy in $Ar^1NO_2H\cdot$ (see below) seems relatively unimportant in comparison with step (4).

2,6-Di-t-butylphenol shows a corresponding CIDNP effect on the ring protons. The results obtained on irradiation in the presence of *p*-dinitrobenzene are shown in Figure 2. The *para*-proton shows enhanced absorption and the *meta*-protons show emission, in agreement with the known signs of the hyperfine splitting of these nuclei in $Ar^2O\cdot$.[5] This observation rules out the transfer of hydrogen from the *p*-methyl of BHT as a source of the nuclear polarization. This conclusion is supported by the following results. (a) The 4-methyl protons of *O*-deuteriated BHT do not undergo deuterium exchange during irradiation in the presence of *p*-dinitrobenzene. (b) The known e.s.r. spectrum of the $Ar^2O\cdot$ free radical of BHT [5] was observed on irradiation of CH_3CN solutions containing both BHT and *p*-dinitrobenzene.

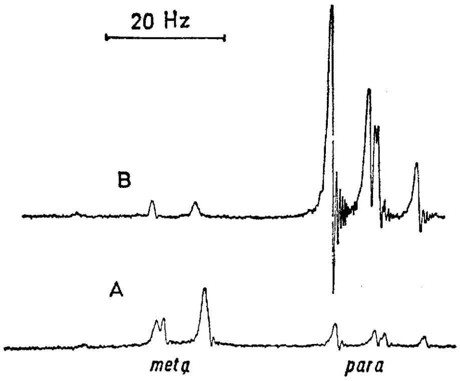


FIGURE 2 90 MHz ^{1}H N.m.r. spectra of ring protons of 2,6-di-t-butylphenol in CD_3CN solution containing both 2,6-di-t-butylphenol and *p*-dinitrobenzene: (A) without u.v. irradiation; (B) during u.v. irradiation. The *para*-^{1}H signal is centred at δ 6.76 and the *meta*-^{1}H at δ 7.13

Though expected, no CIDNP effect on the aromatic protons of the nitro-compounds could be detected in the present systems. This can be attributed both to the low unpaired spin-density located on the ring atoms of $Ar^1NO_2H\cdot$, and to fast nuclear relaxation.[5] The intensity of the CIDNP effect on the *p*-methyl protons of BHT is markedly solvent dependent. This polarization is considerably weaker in CD_3OD solutions and is completely suppressed by the addition of small amounts of H_2O, D_2O, or CD_3O^-. Thus possible competition between hydrogen *versus* electron transfer is indicated, the former only resulting in the CIDNP effect.

No polarization could be observed in $CDCl_3$ or in $C_6D_5NO_2$ solutions, while in C_6D_6 solutions an irreversible photoreduction of the nitro-compounds occurred but no polarization was observed in BHT.

Two threshold features (a) and (b) are clearly discernible in the present systems. These were not observed with xanthen dyes.[2]

(a) The triplet energies E_T of many of the nitro-compounds which abstract hydrogen from BHT are known, the values reported being always larger than 56 kcal mol^{-1}.[4] However, *trans*-4-nitrostilbene (E_T 50 kcal mol^{-1}),[4] 1-nitronaphthalene, and 4-nitroaniline (for both E_T 55 kcal mol^{-1}) [4] fail to show the effect. Thus the value of $E_T = 56$ kcal mol^{-1} for $^3Ar^1NO_2$ represents a threshold below which no hydrogen abstraction from BHT can take place.

(b) In the presence of nitrobenzene (E_T 60 kcal mol^{-1}) [5] no photo-CIDNP effect is observed when BHT is replaced by other phenols such as *p*-cresol or α-tocopherol. The bond dissociation energies of the O–H bond in the sterically hindered phenol BHT is known to be exceptionally low, $D(O{-}H) = 80$ kcal mol^{-1}.[9] This value is lower by *ca.* 10 kcal mol^{-1} than in the unhindered *p*-cresol.[9]

The requirement of exothermicity in step (3) as a condition for hydrogen transfer leads to relationship (5).

$$D(Ar^2O{-}H) - E_T < D(Ar^1NO_2{-}H\cdot) \qquad (5)$$

When (5) is applied to hydrogen abstraction from BHT between the two limits of E_T 57 (transfer) and 55 kcal mol^{-1} (no transfer), we obtain estimate (6). Obviously

$$25 \text{ kcal mol}^{-1} > D(Ar^1NO_2{-}H\cdot) > 23 \text{ kcal mol}^{-1} \qquad (6)$$

the application of (5) for estimating $D(Ar^1NO_2{-}H\cdot)$ remains valid as long as the entropies and the solvation energies of the species taking part in step (1) as well as the Ar^1NO_2 excited states and life-times [4] are reasonably similar for the different Ar^1NO_2–BHT systems.

These conclusions are supported by results obtained with *O*-deuteriated BHT. In this case no effect is obtained with 1,5-dinitronaphthalene (E_T 57 kcal mol^{-1} [5]) as expected from the larger dissociation energy of the O–D bond in *O*-deuteriated BHT due to its lower zero point energy.[9]

---

§ The g values reported for solutions in water–alcohol[7] are lower than $g(ArO\cdot)$.[6a] This apparent contradiction led us to measure directly Δg under the conditions of the CIDNP experiment. Note added in proof: Flow system e.s.r. measurements on u.v.-irradiated 4-nitrobenzonitrile in the presence of BHT also indicate that $g(Ar^1NO_2^{-}\cdot)$ and $g(Ar^1NO_2H\cdot)$ are larger than $g(Ar^2O\cdot)$ (personal communication from Dr. N. Levy).

[6] (*a*) K. Scheffler and H. B. Stegmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 864; (*b*) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **40**, 1815.

[7] C. L. Greenstock, I. Dunlop, and P. Neta, *J. Phys. Chem.*, 1973, **77**, 1187.

[8] R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, 1962, **84**, 306.

[9] L. R. Mahoney, *Angew. Chem. Internat. Edn.*, 1969, **8**, 547.

Thus, it seems that E_T of the aromatic nitro-compounds and D(OH) are decisive factors determining whether hydrogen transfer takes place or not.

The present analysis of the energetics of step (3) may shed light on an important aspect of the photochemistry of nitroaromatic compounds. Aromatic nitro-compounds undergo photochemical reduction by alcohols, ethers, amides, and hydrocarbons.[10] E.s.r. studies of these reactions fail however to provide evidence for the existence of the ('elusive'[10]) $Ar^1NO_2H\cdot$ radical in systems such as nitrobenzene–propan-2-ol or nitrobenzene–tetrahydrofuran. These e.s.r. results are in accord with those of the present work. Thus, whenever the C–H bond energy of the hydrogen atoms to be abstracted is larger than the value of D(O–H) in BHT as in these two cases,[11] we expect the direct hydrogen transfer mechanism as in (3) to be circumvented by reactions which are cheaper in energy such as addition across the N–O bond.*

EXPERIMENTAL

O-Deuteriated BHT was prepared by repeated exchange with D_2O–CD_3OD–DCl solution. CIDNP Measurements were carried out on a Bruker HFX-10 90 MHz spectrometer, equipped with a special optical irradiation probe and quartz insert. Light from a 2 500 W Hanovia mercury–xenon lamp was led horizontally to the sample through a 5 mm O.D. quartz light guide. Concentrations within the range 0.05—0.5M of both nitro-compound and of phenol derivative were examined. Within this range no dependence of the CIDNP effect on the concentration was observed. The usual ^1H sweep range of 0—12 p.p.m. *versus* tetramethylsilane (TMS) was examined in every experiment. Though experiments were usually carried out in the absence of TMS, no hydrogen abstraction from TMS (whenever present) could be observed. In the systems described no other CIDNP peak (including short lifetime peaks) were observed. E.s.r. measurements were carried out on a Varian E-3 spectrometer. Samples were irradiated inside the cavity with an Osram HBO-200 mercury lamp. E.s.r. spectra of the nitrobenzene anion radical were obtained by irradiation of CH_3CN solutions of nitrobenzene and BHT (both 0.1M, no outgassing). The spectrum of the BHT radical could be observed in irradiated CH_3CN solutions containing both BHT and Rose Bengal (0.1 and 0.001M respectively, no outgassing).[2] A CH_3CN solution containing BHT (0.1M), nitrobenzene (0.01M), and Rose Bengal (0.001M) when irradiated gave the superimposed spectra of both radicals from which Δg could be directly determined.

No CIDNP could be detected when samples were irradiated outside of the n.m.r. probe.

We thank Mr. M. Grinberg for the n.m.r. measurements.

[5/2062 *Received*, 21*st October*, 1975]

---

* A medium effect has been suggested by a referee as an additional factor which could be responsible for some of the e.s.r. observations. Thus in propan-2-ol and tetrahydrofuran disproportionation of $PhNO_2H\cdot$ could give $PhN(OH)_2$ and hence PHNO which could act as radical scavenger.

[10] S. K. Wong and J. K. S. Wan, *Canad. J. Chem.*, 1973, **51**, 753 and references cited therein.

[11] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.