

# Water-Assisted Intramolecular Electron Transfer from the Ring to the Side Chain in *N,N,N',N'*-Tetraalkyl-*para*-phenylenediamine Radicals—The Reverse of Side Chain Deprotonation of Radical Cations

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For arenes containing (substituted) alkyl groups as substituents, “activation” of the side chain is often possible by changing the “oxidation state” of the arene, for example, by one-electron reduction,<sup>[1–7]</sup> or more often, one-electron oxidation.<sup>[8–13]</sup> A very characteristic process for the side chain reactivity of radical cations is deprotonation from carbon which leads typically to (neutral) benzyl-type radicals. The reciprocal reaction, protonation on carbon, has also been observed (with radical anions),<sup>[14–20]</sup> but it typically takes place *not* on the side chain but on the ring. We have now found evidence for the protonation of a side chain carbon atom (a reaction which involves a neutral radical), electron transfer from the ring to the side chain providing the (high) electron density necessary for the protonation on carbon to occur.

N<sub>2</sub>O-saturated aqueous solutions at pH 7–12 containing *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD; used as the dihydrochloride) were irradiated with the 100 ns pulses from a 3 MeV van de Graaff electron accelerator, and the time-resolved changes in the transmission or of the conductance of the solution monitored. Irradiation of water leads to the radicals  $\cdot\text{OH}$  (45 %),  $\text{H}\cdot$  (10 %), and  $\text{e}_{\text{aq}}^-$  (45 %). The latter reacts with N<sub>2</sub>O within 20 ns to yield another  $\cdot\text{OH}$  radical. In the presence of 0.2–0.5 mM TMPD, its radical cation  $\text{TMPD}^{+\cdot}$  is produced, whose  $\lambda_{\text{max}}$  values are at 330, 565, and 610 nm (Figure 1).<sup>[21, 22]</sup>  $\text{TMPD}^{+\cdot}$  is formed by two routes, a direct and an indirect one. The direct (“fast”) reaction accounts for (55 ± 5) % of the total formation of  $\text{TMPD}^{+\cdot}$  (Figure 1, inset b). The rate, but not the yield, of this reaction depends on the concentration [TMPD],<sup>[23]</sup> whereas the rate of the second, slower reaction ( $k = (6.6 \pm 1) \times 10^4 \text{ s}^{-1}$  at 20 °C<sup>[24]</sup>) turned out to be independent of [TMPD] (0.1–1 mM) and pH (7–12), but dependent on temperature (between 0 and 50 °C), the resulting Eyring parameters for the electron transfer and side chain protonation (see Scheme 2) being  $\Delta H^\ddagger = (4.9 \pm 0.5) \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = (-19 \pm 1.6) \text{ cal mol}^{-1} \text{ K}^{-1}$ . Furthermore at pH 8–11 the reaction of  $\cdot\text{OH}$  with TMPD leads to an increase in conductance of the solution (Figure 1, inset c) assignable<sup>[25]</sup> to the formation of an organic (radical) cation and the OH<sup>−</sup> ion, again in a two-step process, as observed with optical detection. The rate of the slow process and the step height of the change in conductance were independent of the pH value (8–11)<sup>[26]</sup> and of the [TMPD] (0.1–1 mM), and were

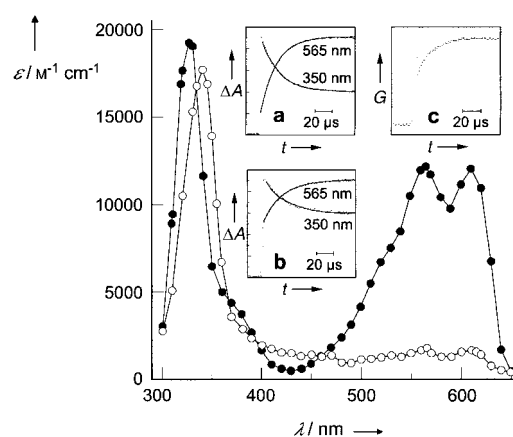


Figure 1. Absorption spectra recorded after reaction of  $\text{O}^{\cdot-}$  with 0.4 mM TMPD in N<sub>2</sub>O-saturated water ([KOH] = 0.4 M, 20 °C). ● = spectrum of  $\text{TMPD}^{+\cdot}$ , ○ = spectrum of  $>\text{NCH}_2\cdot$ . Insets a and b show the decay of  $>\text{NCH}_2\cdot$  (350 nm) and the build up of  $\text{TMPD}^{+\cdot}$  (565 nm) at 0.4 M KOH and pH 7.4, respectively. Inset c shows the increase in conductance *G* at pH 10, which primarily reflects the formation of OH<sup>−</sup>.

equal (within 10 %) with those optically measured (compare with inset b).

On replacement of  $\cdot\text{OH}$  by  $\text{O}^{\cdot-}$ , the conjugate base of  $\cdot\text{OH}$  ( $\text{p}K_{\text{a}}(\cdot\text{OH}) = 11.9$ ), the height of the initial step at 565 nm (see insets) was found to be much smaller than at pH 7–8.<sup>[27]</sup> Under these conditions,<sup>[28]</sup> the first process contributed only 15 % of the total formation of  $\text{TMPD}^{+\cdot}$ , and the main reaction was the slow formation of  $\text{TMPD}^{+\cdot}$  with  $k = 6.0 \times 10^4 \text{ s}^{-1}$ , that is with essentially the same rate constant as for the reaction at pH 7–12, where, however,  $\cdot\text{OH}$  is the reactant.

Based on the fact that  $\text{O}^{\cdot-}$  reacts with arenes typically by H-abstraction from the side chain,<sup>[29]</sup> the side-chain-derived radical  $>\text{NCH}_2\cdot$  is expected to be formed in its reaction with TMPD (see Scheme 1). Similar to other  $\alpha$ -aminoalkyl-type radicals,<sup>[30]</sup>  $>\text{NCH}_2\cdot$  should be a good one-electron reducing agent, and this was in fact found to be the case since this radical could be scavenged by the mild oxidant methylviologen ( $\text{MV}^{2+}$ ) to yield  $\text{MV}^{+\cdot}$  ( $k = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The yield of  $>\text{NCH}_2\cdot$ , determined at pH 9 with this method,<sup>[31]</sup> is 53 % relative to the initial  $\cdot\text{OH}$  present. This value is in agreement with the numbers derived from the optical and conductance step heights (Figure 1, insets b and c).

The reaction of  $\cdot\text{OD}$  with TMPD in heavy water (D<sub>2</sub>O) also led to the formation of  $\text{TMPD}^{+\cdot}$  in two steps. However, the rate constant for the second, slow process, which is assigned to the conversion of  $>\text{NCH}_2\cdot$  to  $\text{TMPD}^{+\cdot}$  (see Scheme 2), was smaller than that for the reaction in H<sub>2</sub>O by the factor 3.0; thus, the solvent kinetic isotope effect (KIE) is 3.0, a value that is consistent with the (heterolytic) rupture of an O–H bond in the transition state. The activation entropy of  $-19 \text{ cal mol}^{-1} \text{ K}^{-1}$  is in agreement with this concept, since motional degrees of freedom are lost by participation of a water molecule in the transition state of the intramolecular electron transfer from the ring to the side chain.

To study the effect of the alkyl substituent on the amino nitrogen atom of the *para*-phenylenediamine moiety, the OH radical was also allowed to react with the *N,N,N',N'*-tetraethyl and *n*-propyl derivatives. As with TMPD, the corresponding radical cations were formed in two steps; the yields for the

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“fast” (bimolecular) reaction were 70–80%.<sup>[32]</sup> The subsequent unimolecular reaction revealed  $k$  values of  $1.2 \times 10^4$  and  $7.1 \times 10^3 \text{ s}^{-1}$  for the ethyl<sup>[33]</sup> and  $n$ -propyl derivatives, respectively. Figure 2 shows a Taft plot ( $\sigma^*$  values) of the rate

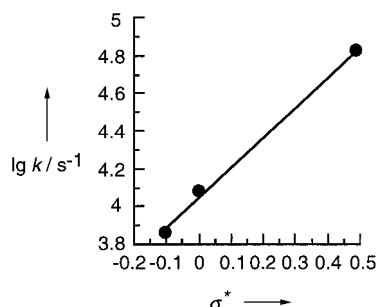
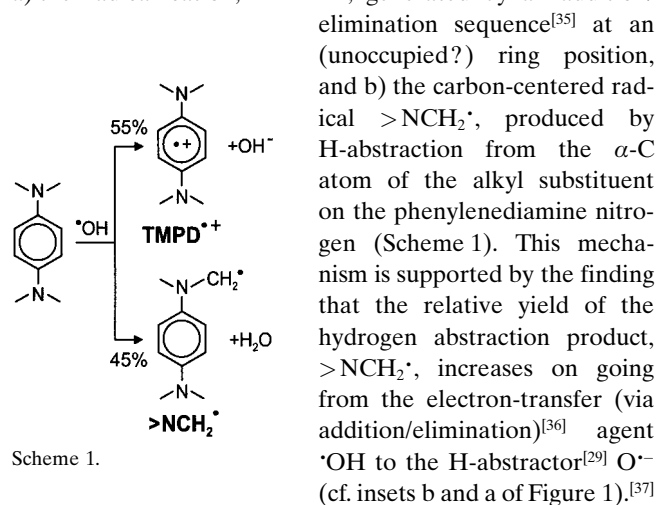


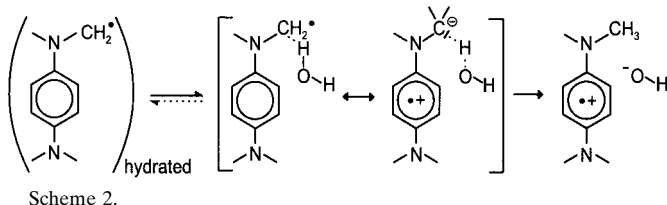
Figure 2. Taft plot of the transformation of  $>\text{NCH}_2\text{R}$  ( $\text{R} = \text{H, Me, Et}$ ) into the corresponding radical cation. The Taft parameter was determined to be  $\rho^* = 1.6$  from the slope.

constants for the transformations of the  $\alpha$ -aminoalkyl-type radicals into the corresponding phenylenediamine radical cations. The deceleration of the reaction on going from Me to  $n\text{Pr}$ , reflected in the positive apparent  $\rho^*$  value of 1.6, may be due to an increase of electron density at the carbon carrying the unpaired electron<sup>[34]</sup> or to steric effects.

On the basis of the experimental data presented, a mechanism is suggested which involves the formation of two different radicals from the reaction of  $\cdot\text{OH}$  with TMPD:



Clearly, for the “unimolecular” transformation of  $>\text{NCH}_2\cdot$  to  $\text{TMPD}^{\cdot+}$  a proton donor is necessary, and it is proposed that a water molecule serves this purpose. The mechanism suggested (Scheme 2) involves the transfer of an electron from the ring to the N-substituted alkyl



radical; a water molecule acts as the protonating agent<sup>[38, 39]</sup> (and possibly as an electron transfer mediator) in the transition state of the electron transfer. Evidence for this comes from the kinetic isotope effect of 3 and the negative activation entropy. The anion complementary to the radical cation is  $\text{OH}^-$ , and this was detected directly (as a hydrated ion) by time-resolved measurement of the conductance (see Figure 1, inset c).

To summarize, evidence has been presented for a water-assisted intramolecular transfer of an electron from the ring as the electron donor to a carbon-centered radical located on the side chain at a position  $\beta$  to the ring as the (weak!) electron acceptor. Formally, the result of this electron transfer would be a *carbanion* on the side chain. However, as concluded from the solvent kinetic isotope effect which indicates the breakage of an O–H bond in the transition state of the electron transfer, protonation by water of this carbon atom is concerted with the electron transfer. The (new) mechanism presented in Scheme 2, which corresponds to the reverse of side chain deprotonation<sup>[40]</sup> of radical cations,<sup>[41]</sup> is an example of the importance of proton transfer in electron transfer processes in aqueous solution.

### Experimental Section

The pulse radiolysis experiments were performed by using a 3 MeV van de Graaff accelerator which supplied 100 ns pulses with doses such that radicals were produced in concentrations of 0.5–3  $\mu\text{M}$ . A thermostatable quartz flow cell, typically set at 20°C, was employed in all experiments. Dosimetry was done with  $\text{N}_2\text{O}$ -saturated 10 mM KSCN solutions taking  $G(\cdot\text{OH}) = 6.0 \times 10^{-7} \text{ mol J}^{-1}$  and  $\epsilon[(\text{SCN})_2^{\cdot-}] = 7600 \text{ M}^{-1} \text{ cm}^{-1}$  at 480 nm.<sup>[42]</sup> The solutions were prepared by dissolving the tetraalkyl- $p$ -phenylenediamine dihydrochlorides in water deoxygenated with  $\text{N}_2\text{O}$  and then adjusting the pH to  $\geq 7$  by addition of KOH or  $\text{Na}_2\text{HPO}_4$ . The radiation-induced changes of the solution were digitized and analyzed by an on-line DEC-PDP 11/73+ computer system which also controlled the apparatus and pre-analyzed the data. For the time-resolved conductance changes, an AC system with 1  $\mu\text{s}$  time resolution was used.

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- [1] P. Neta, D. Behar, *J. Am. Chem. Soc.* **1980**, *102*, 4798–4802.
- [2] P. Neta, D. Behar, *J. Am. Chem. Soc.* **1981**, *103*, 103–106.
- [3] D. Behar, P. Neta, *J. Am. Chem. Soc.* **1981**, *103*, 2280–2283.
- [4] D. Behar, P. Neta, *J. Phys. Chem.* **1981**, *85*, 690–693.
- [5] P. Maslak, J. N. Narvaez, *J. Chem. Soc. Chem. Commun.* **1989**, 138–139.
- [6] J. M. Saveant, *Acc. Chem. Res.* **1993**, *26*, 455–461.
- [7] J. M. Saveant in *Advances in Electron Transfer Chemistry*, Vol. 4, (Ed.: P. S. Mariano), Jai, Greenwich, CO, **1994**, pp. 53–116.
- [8] A. M. D. Nicholas, D. R. Arnold, *Can. J. Chem.* **1982**, *60*, 2165–2179.
- [9] S. Steenken, R. A. McClelland, *J. Am. Chem. Soc.* **1989**, *111*, 4967–4973.
- [10] S. Steenken, C. J. Warren, B. C. Gilbert, *J. Chem. Soc. Perkin Trans. 2* **1990**, 335–342.
- [11] P. Maslak, J. N. Narvaez, *Angew. Chem.* **1990**, *102*, 302–304; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 283–285.
- [12] M. Schmittle, A. Burghart, *Angew. Chem.* **1997**, *109*, 2658–2699; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2550–2589.
- [13] a) E. Baciocchi, M. Bietti, L. Manduchi, S. Steenken, *J. Am. Chem. Soc.* **1999**, *121*, 6624–6629; b) M. Bietti, S. Steenken in *Handbook of Electron Transfer in Chemistry* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**, in press.
- [14] R. W. Fessenden, O. P. Chawla, *J. Am. Chem. Soc.* **1974**, *96*, 2262–2263.

- [15] R. H. Schuler, P. Neta, H. Zemel, R. W. Fessenden, *J. Am. Chem. Soc.* **1976**, *98*, 3825–3831.
- [16] D. J. Deeble, S. Das, C. von Sonntag, *J. Phys. Chem.* **1985**, *89*, 5784–5788.
- [17] H. M. Novais, S. Steenken, *J. Am. Chem. Soc.* **1986**, *108*, 1–6.
- [18] S. Steenken, J. P. Telo, H. M. Novais, L. P. Candeias, *J. Am. Chem. Soc.* **1992**, *114*, 4701–4709.
- [19] L. P. Candeias, P. Wolf, P. O'Neill, S. Steenken, *J. Phys. Chem.* **1992**, *96*, 10302–10307.
- [20] L. P. Candeias, S. Steenken, *J. Phys. Chem.* **1992**, *96*, 937–944.
- [21] S. Fujita, S. Steenken, *J. Am. Chem. Soc.* **1981**, *103*, 2540–2045.
- [22] The total yield of TMPD<sup>•+</sup> was 100% as calibrated by the reaction of TMPD with (SCN)<sub>2</sub><sup>•-</sup>, whose yield (in 10 mM KSCN) is equal to that of <sup>•</sup>OH, see: R. H. Schuler, L. K. Patterson, E. Janata, *J. Phys. Chem.* **1980**, *84*, 2088.
- [23] From the dependence on [TMPD] of the rate of formation of TMPD<sup>•+</sup> in the initial direct, “fast” reaction the rate constant for its formation by <sup>•</sup>OH is  $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The same value was obtained from an experiment where 2-propanol competed with TMPD for <sup>•</sup>OH (with  $k(\text{OH} + i\text{PrOH}) = 2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).
- [24] All rate constants given in the paper refer to  $(20 \pm 0.2)^\circ\text{C}$ .
- [25] The time-resolved AC method was used. Dosimetry was performed with the reaction <sup>•</sup>OH and *N,N*-dimethylaniline which yielded *N,N*-dimethylaniline<sup>•+</sup> and OH<sup>-</sup>: J. Holcman, K. Sehested, *J. Phys. Chem.* **1977**, *81*, 1963.
- [26] This also shows that TMPD<sup>•+</sup> does not react with OH<sup>-</sup>, as also concluded from the independence of the lifetime of TMPD<sup>•+</sup> on [OH<sup>-</sup>].
- [27] In contrast, the absorption at 350 nm was much higher than that at pH 7–8 (cf. insets a, b in Figure 1).
- [28] Using 0.2–0.5 mM TMPD and 0.4–0.5 M KOH.
- [29] P. Neta, R. H. Schuler, *Radiat. Res.* **1975**, *64*, 233.
- [30] See, for example: S. Steenken and V. Jagannadham, *J. Am. Chem. Soc.* **1985**, *107*, 6818, and references therein.
- [31] For calibration an N<sub>2</sub>O-saturated solution of 10 mM sodium formate and 0.5 mM MV<sup>2+</sup> was used (yield of MV<sup>•+</sup>  $\equiv$  100%).
- [32] As calibrated by reaction with (SCN)<sub>2</sub><sup>•-</sup>. However, the total yield of radical cation was less than 100%, indicating H-abstraction from terminal carbon atoms in the alkyl groups.
- [33] In the case of tetraethyl-*p*-phenylenediamine, the activation parameters were measured for the intramolecular formation of radical cation:  $\Delta H^\ddagger = 6.2 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -19 \text{ cal mol}^{-1} \text{ K}^{-1}$ .
- [34] Alkyl substitution at C<sub>a</sub> leads to stabilization of the radical and thus disfavors the transformation to the aromatic radical cation.
- [35] With  $k_{\text{elimination}} \geq 3 \times 10^6 \text{ s}^{-1}$ .
- [36] S. Steenken, *J. Chem. Soc. Faraday Trans. 1* **1987**, *83*, 113–124.
- [37] The conceivable alternative that the radical which undergoes the transformation reaction to TMPD<sup>•+</sup> is the *ipso*-OH adduct, is thereby excluded, since the yield of the *ipso*-OH adduct would decrease on going from <sup>•</sup>OH to O<sup>•-</sup>.
- [38] The thermodynamic acidity of TMPD<sup>•+</sup> is not known. However, on the basis of the observation that even in 1 M KOH, TMPD<sup>•+</sup> persists, its pK<sub>a</sub> value is estimated to be  $\gg 14$  which is in line with the conjugate base,  $>\text{NCH}_2^\cdot$ , being protonatable by H<sub>2</sub>O.
- [39] The conversion of  $>\text{NCH}_2^\cdot$  into TMPD<sup>•+</sup> can be accelerated by phosphate: For this reaction at pH 8,  $k = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (determined from the linear dependence of  $k_{\text{obs}}$  on [phosphate]).
- [40] E. Baciocchi, M. Bietti, O. Lanzalunga, *Acc. Chem. Res.* **2000**, *33*, 243–251.
- [41] The basis for the electron transfer from the ring to the side chain lies in the very high electron density at the ring which is enhanced through the second dialkylamine function. In line with this, the reaction corresponding to that in Scheme 2 does not take place for the analogous  $\alpha$ -aminoalkyl radical of *N,N*-dimethylaniline.
- [42] R. H. Schuler, A. L. Hartzell, B. Behar, *J. Phys. Chem.* **1981**, *85*, 192–199.

## Liquid-Phase Synthesis of Colloids and Redispersible Powders of Strongly Luminescing LaPO<sub>4</sub>:Ce,Tb Nanocrystals\*\*

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An increasing number of nanocrystalline materials have been synthesized in high-boiling coordinating solvents, since binding of the solvent molecules to the particle surface leads to colloidal solutions of well-separated particles.<sup>[1]</sup> If process parameters such as concentration and temperature are properly adjusted<sup>[2]</sup> and, most importantly, a suitable solvent for the reaction is found, colloidal solutions of highly crystalline nanoparticles with very narrow particle size distributions are the result. Examples for this method are the synthesis of high-quality cadmium chalcogenide nanoclusters<sup>[1a]</sup> and TiO<sub>2</sub> nanoclusters<sup>[1b]</sup> in trioctylphosphine oxide (TOPO) and the preparation of InP<sup>[1c,d]</sup> and InAs nanoclusters<sup>[1e]</sup> in trioctylphosphane (TOP). Similarly, ZnSe,<sup>[1f]</sup> Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>4</sub>, and Cu<sub>2</sub>O nanoclusters<sup>[1g]</sup> have been prepared in long-chain alkylamines. Our synthesis of LaPO<sub>4</sub>:Eu and CePO<sub>4</sub>:Tb in tris-ethylhexylphosphate<sup>[1h]</sup> shows that the method is also applicable to *doped* nanoparticles.

Oxide materials form the active material of most solid-state lasers and are technologically important as phosphors in cathode ray tubes, X-ray detectors, and in lighting applications.<sup>[3]</sup> The latter group includes the mixed phosphate La<sub>0.40</sub>Ce<sub>0.45</sub>Tb<sub>0.15</sub>PO<sub>4</sub>, which is used in luminescent lamps as highly efficient emitter of green light.<sup>[4]</sup> The material is chemically very stable, even in the presence of the mercury plasma discharge inside the lamp, and has an overall luminescence quantum yield of 93%.<sup>[5]</sup> Redispersible nanoparticles of La<sub>0.40</sub>Ce<sub>0.45</sub>Tb<sub>0.15</sub>PO<sub>4</sub> may therefore form a stable and efficient substitute for organic laser dyes in various applications. In fact, semiconductor nanoparticles such as CdSe have successfully been applied, for instance, as luminescing labels for biomolecules<sup>[6]</sup> and as light-emitting molecular substances in electroluminescent devices.<sup>[7]</sup>

Herein we present an improved synthesis that yields more than 10 grams of the ternary system La<sub>0.40</sub>Ce<sub>0.45</sub>Tb<sub>0.15</sub>PO<sub>4</sub> in a simple one-pot reaction which does not involve rapid mixing of dissolved compounds. Rapid mixing at elevated temperatures is often applied to separate nucleation and growth of the nanoparticles,<sup>[8]</sup> but becomes increasingly difficult with larger amounts of reactants. Nevertheless, our procedure yields a remarkably narrow particle size distribution even on this preparative scale. This is shown by transmission electron

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