Transfer Hydrogenation of Nitro-, Nitroso- and Azoarenes by Homolytic Retrodisproportionation**

Michael Coellen and Christoph Rüchardt*

Dedicated to Prof. Dr. Manfred Schulz on the occasion of his 65th birthday

Abstract: Nitro-, nitroso- and azobenzene are reduced almost quantitatively to aniline when heated to 230–300 °C with 9,10-dihydroanthracene (DHA), xanthene or tetralin. From the effect of polar substituents and polar solvents on the reactivity and from the isotope effect $k_H/k_D \approx 2.4$ (280 °C), a hydrogen-atom transfer from the H donor to the acceptor (*retrodisproportionation*) is proposed as the rate-determining step. The lower reactivity of xanthene compared with 9,10-dihydroanthracene eliminates the possibility of a rate-determining hydride transfer. The observation of an intense ESR signal of 9-xanthyl radicals during the reaction in diphenyl ether and the typical products support the proposed homolytic mechanism.

Keywords
aniline · aromatization · hydrogen transfer · mechanistic studies · radicals

Introduction

The uncatalyzed transfer of hydrogen atoms from 9,10-dihydroanthracene (DHA),[2] xanthene,[2] fluorene,[3] acridane[4] and other H donors D–H with weak C–H bonds[3] to α-methylstyrene and other unsaturated H acceptors[5] X=Y–A in a *retrodisproportionation* reaction [Eq. (1)] was recently[1–6]

$$D\text{-}H + X\text{=}Y\text{-}A \xrightarrow{T} D^{\cdot} + HX\text{-}\dot{Y}\text{-}A \xrightarrow[-2D]{+DH} HX\text{-}YH\text{-}A \qquad (1)$$

recognized as the first step of many uncatalyzed H transfer reactions at high temperatures. It is followed by an H abstraction step and by disproportionation or dimerization of the donor radicals D·. These nonchain homolytic reactions seem to be important in coal liquefaction processes[7] and they are a potential new initiator system for radical polymerization.[8]

We now turn to the question of whether other H transfer processes, such as the well-known dehydrogenation and aromatization reactions of cyclic alkenes with nitrobenzene[9a] or quinones[9–10] as H acceptors, are likewise initiated by H atom transfer and retrodisproportionation instead of the ionic hydride transfer or electron transfer generally postulated.[9–11] Classic examples for dehydrogenations with nitrobenzene are the final steps of the Skraup, Doebner–Miller or Bischler–Napieralski syntheses of quinolines or isoquinolines.[12] The scope of nitrobenzene dehydrogenations has not been previously explored.

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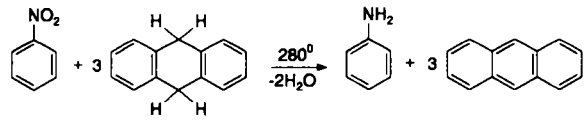
[**] Bimolecular Formation of Radicals by H Transfer, Part 8; Part 7: see ref. [1]. The present paper is taken from the diploma thesis of M. Coellen, University of Freiburg **1994**.

Results and Discussion

Transition metal catalyzed reductions of nitrobenzene to aniline by alcohol,[13] formic acid[14] and hydroaromatics[15] are well-known processes.[16] We have observed that, contrary to information in the literature,[15] nitrobenzene is *almost quantitatively* reduced to aniline when heated *without a catalyst* to 250–300 °C with an excess of DHA (Scheme 1) (see Table 1, entries 1–6).



Scheme 1.

DHA alone is stable at these temperatures.[3] The reaction has first-order kinetics with respect to nitrobenzene but only 0.6–0.7th order with respect to DHA. It was therefore investigated with an excess of DHA under pseudo-first-order conditions. Because it is not known whether the reaction order with respect to the H donor depends on the type or the concentration of the donor, the temperature or the solvent, the activation parameters are not presented here, and structural reactivity data are discussed only on the basis of half-lives under pseudo-first-order conditions, mostly in a semiquantitative way. The stoichiometry of the reductions is as expected: three equivalents of anthracene are generated. Nitrosobenzene is detected by GC as a transient intermediate (Fig. 1). The half-life of the reaction is apparently little affected by the polarity of the solvent (Table 1, entries 5, 7–10) and independent of an added radical initiator (Table 1, entries 5, 16); this makes either hydride or electron transfer or a chain mechanism improbable. The fact that the rate is 28 times faster in *N*-methylacetamide ($E_T(30) = 52$)[17] than in di-

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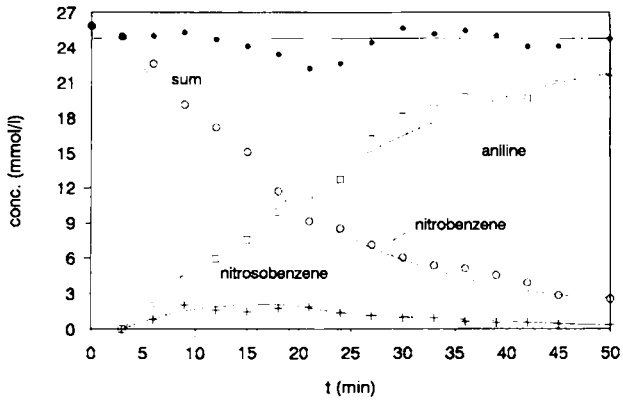
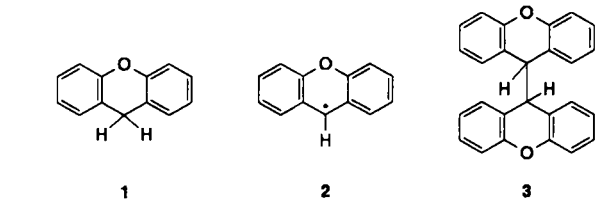


Fig. 1. Time dependence of product concentrations and mass balance during the transfer hydrogenation of nitrobenzene (27 mM) with DHA (0.96 M) in diphenyl ether at 280 °C.

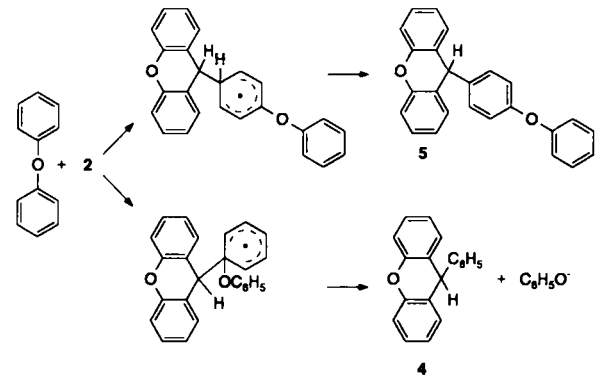
chlorobenzene ($E_T(30) = 38$)[17] rules out a rate-determining hydride transfer. For S_N1 ionization reactions, differences in rate of approximately 10^5 have been found for similar changes in ionization power of the solvent.[18] Substituents in the aromatic ring of nitrobenzene have only a small influence on the rates (Table 1, entries 11–14)[3b] (with no relationship to σ constants). When [9,9,10,10-D_4]DHA (DDHA) is used for the reduction of nitrobenzene at 280 °C, a kinetic isotope effect is observed, $k_H/k_D \approx 2.4$ (Table 1, entry 15), which is comparable to the isotope effects of other homolytic H transfer reactions.[2, 3]

The hydrogenation of nitrosobenzene to aniline is even faster; azoxybenzene and probably phenylhydroxylamine are intermediates (Table 1, entries 20, 21). Under similar conditions azobenzene is also reduced to aniline quite rapidly (Table 1, entry 22).

When xanthene (**1**) is used as the hydrogen source then 9,9′-bixanthene (**3**) is the dominant oxidation product, typical for a radical process[2] (Table 1, entry 17). An intense ESR spectrum of 9-xanthyl radicals (**2**) is seen when the reaction is conducted in the cavity of an ESR spectrometer (see also ref. [2]); this observation supports a radical mechanism. However, aniline is formed in only 25% yield, while two further products are detected in 25% and 50% yield (GC); these are products of 9-xanthyl and phenylaminyl radicals (GC-MS) (probably 9-(*o*-aminophenyl)- and 9-(*p*-aminophenyl)xanthene), respectively. In addition 9-phenylxanthene (**4**) and 9-(*p*-phenoxy)phenylxanthene (**5**) are detected by GC-MS in amounts comparable to aniline. They are believed to be formed when 9-xanthyl radicals (**2**) attack the solvent (Scheme 2). When nitrobenzene is reduced by



1 **2** **3**



Scheme 2.

Table 1. Transfer hydrogenation of nitro-, nitroso- and azoarenes.

Entry	H acceptor (mM)	H donor [a] (M)	Solvent [b]	T (°C)	$t_{1/2}$ [c] (min)	Products [d] (% yield)
1	nitrobenzene (27) [e]	DHA (0.96)	de	255	80	ani (95), ant (305)
2	nitrobenzene (27)	DHA (0.96)	de	260	56	ani (95), ant (305)
3	nitrobenzene (27)	DHA (0.96)	de	265	38	ani (95), ant (305)
4	nitrobenzene (27)	DHA (0.96)	de	275	16	ani (95), ant (305)
5	nitrobenzene (27)	DHA (0.96)	de	280	14	ani (95), ant (305)
6	nitrobenzene (27)	DHA (0.96)	de	285	10	ani (95), ant (305)
7	nitrobenzene (27)	DHA (0.96)	xy	280	11	ani (95), ant (305)
8	nitrobenzene (27)	DHA (0.96)	db	280	56	ani (95), ant (320)
9	nitrobenzene (27)	DHA (0.96)	bn	280	52	ani (95), ant (305)
10	nitrobenzene (27)	DHA (0.96)	na	280	2	ani (97), ant (280)
11	*p*-Cl-nitrobenzene (27)	DHA (0.96)	de	275	24	*p*-chloroaniline (97), ant (300)
12	*p*-nitrotoluene (27)	DHA (0.96)	de	275	27	*p*-toluidine (93), ant (265)
13	*p*-nitrobenzonitrile (27)	DHA (0.96)	de	275	10	*p*-aminobenzonitrile, ant (300)
14	*p*-nitroanisole (27)	DHA (0.96)	de	275	69	*p*-anisidine (96), ant (290)
15	nitrobenzene (28)	DDHA (0.86)	de	280	51	ani (95)
16	nitrobenzene (27) [f]	DHA (0.96)	de	280	16	ani (99), ant (300)
17	nitrobenzene (27)	xanthene (0.96)	de	265	67	ani (25), 3 (180)
18	nitrobenzene (50)	xanthene (1.00)	mes	265	118	ani (93), see Fig. 2
19	nitrobenzene (28)	tetralin (1.02)	de	300	22	ani (99), bitetralyl, naphthalene
20	nitrosobenzene (27) [g]	DHA (0.96)	de	280	$\ll 2$	ani (98), ant (200)
21	nitrosobenzene (34)	DHA (0.55)	de	210	33	ani (98), ant (200)
22	azobenzene (50)	DHA (1.0)	de	230	23	ani (80), ant (195)
23	nitrocyclohexane (27)	DHA (0.96)	de	280	180	cyclohexane (100), ant

[a] DHA = 9,10-dihydroanthracene; DDHA = [9,9,10,10-D_4]DHA. [b] Solvents: de = diphenyl ether; xy = *p*-xylene, db = 1,2-dichlorobenzene; bn = benzonitrile; na = *N*-methylacetamide, mes = mesitylene. [c] $t_{1/2}$ = half-life of the decrease in H acceptor concentration (the rate of the H transfer is first order with respect to the H acceptor concentration). [d] ani = aniline; ant = anthracene; if no yield is reported, a quantitative analysis of the products was prevented by overlap of peaks. However, GC yields were in the 90% range in all cases. [e] Nitrosobenzene could be observed as an intermediate product. [f] Addition of 50 mol% of 9,9′-bifluorene (13.5 mM) relative to nitrobenzene. [g] Azoxybenzene could be observed as an intermediate product.

xanthene in mesitylene at 265 °C (Table 1, entry 18) then aniline is obtained in 93% yield with a reaction half-life of 118 min. During the reaction the concentration of 9,9'-bixanthene (**3**) builds up and disappears[19] again (see Fig. 2). In addition approximately 8% 9-(3,5-dimethyl)benzylidenexanthene is formed (GC-MS) besides the dominant final product, 9-mesitylxanthene (3 molequiv, see Fig. 2). Under these conditions the solvent slowly transfers hydrogen to the radicals **2**, generating

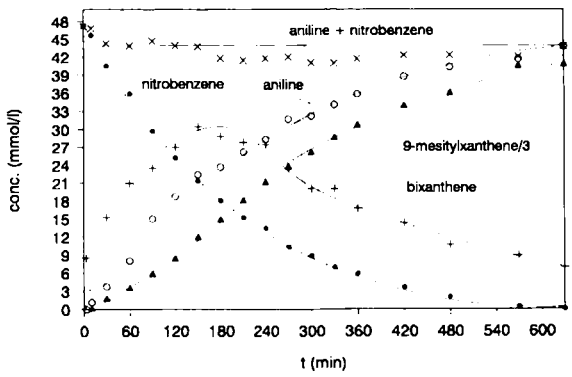
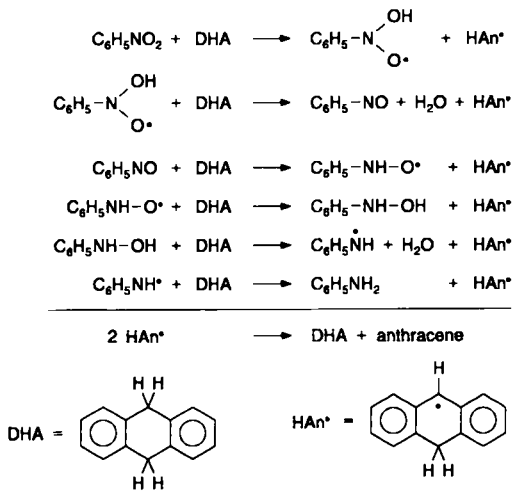


Fig. 2. Time dependence of product concentrations and mass balance during the transfer hydrogenation of nitrobenzene (50 mM) with xanthene (1 M) in mesitylene at 265 °C.

mesityl radicals. The latter react with xanthyl radicals. The solvent mesitylene itself is also oxidized by nitrobenzene at 265 °C, but much more slowly. With a reaction half-life of 449 min aniline is formed (33%) alongside mesityl alcohol (40%), 3,5-dimethylbenzaldehyde (70%), *N*-(3,5-dimethylbenzylidene)-aniline (27%), *N*-mesitylaniline (16%) and bimesityl (< 5%); the yields (GC-MS) refer to the input of nitrobenzene and 20 h reaction time.

Besides the transfer hydrogenation of nitro-, nitroso-, azoxy- and azobenzene, transfer hydrogenolysis of hydrazobenzene and phenylhydroxylamine must also be assumed. We propose that the *basic* mechanism depicted in Scheme 3 is operating.

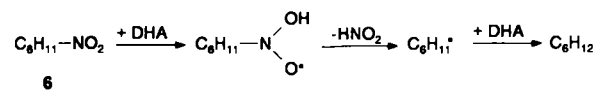
The mechanism is probably even more complicated than Scheme 3 indicates because the various nitroxide radicals can also react (reversibly) with each other or with hydroanthryl radicals HAn$^{\bullet}$ or other radicals derived from H donors. These



Scheme 3. Mechanism proposed for the dehydrogenation of DHA by nitrobenzene and nitrosobenzene.

additional reactions are probably also responsible for the observed deviations from second-order behaviour. We are now carrying out detailed investigations of the transfer hydrogenation of the isolated intermediates of Scheme 3, hydrazobenzene, azobenzene, azoxybenzene and nitrosobenzene, to obtain more information concerning this question.

When heated with DHA to 280 °C, nitrocyclohexane **6** is reduced cleanly but more slowly than nitrobenzene to cyclohexane, without detectable by-products. The mechanism in Scheme 4, which has some similarity to the tin hydride reduction,[20] is proposed. Work is in progress to explore the scope of this new hydrodenitration procedure.



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Scheme 4.

Conclusions

The lack of large polar substituent and solvent effects, the observed kinetic order and isotope effect and the ESR evidence all imply that dehydrogenation of hydroaromatic compounds, and possibly others, by nitrobenzene follows a homolytic nonchain H transfer mechanism with an initiating *retrodisproportionation* step as previously observed in other cases.[1, 2, 3, 21] In the reduction cascade ending with aniline, transfer hydrogenolysis steps[22] may also be involved, for example as in Equation 2:

$$C_6H_5-NH-NH-C_6H_5 + DHA \longrightarrow C_6H_5\dot{N}H + C_6H_5NH_2 + HAn^{\bullet} \quad (2)$$

but unimolecular homolysis of hydrazobenzene cannot be excluded at this time. Interference of longer-lived nitroxide radical intermediates probably makes the reaction scheme leading finally to aniline more complicated.

Work is in progress to test the scope of these transformations and the proposed mechanisms. Similar results will soon be reported for quinone dehydrogenation reactions.[9b]

Experimental Procedure

GC: Carlo-Erba fractometer GC6000, Vega Series 2 with FID; Carlo-Erba Autosampler CTC-A200; capillary column SE 30/25m with an inner diameter of 0.32 mm and a layer thickness of 0.25 μm, N_2 flow 2 mL min^{-1}; GC-MS: Varian fractometer 3700; Finnigan MAT 44s; thermolysis: tin thermostat (constructed in laboratory); electronic temperature control unit: Oxford Electronic Instruments DTC/CK01; temperature measurement: Systemtechnik AB Pt100/S1220.

Most chemicals and solvents were commercially available and purified by fractional distillation or crystallization to ≥99% purity; the substituted nitrobenzenes and anilines were purified by distillation. [9,9,10,10-D_4]dihydroanthracene was prepared as described elsewhere [21a].

Thermolysis: A solution of 9,10-dihydroanthracene (3.3 mmol), nitrobenzene (100 μmol) and *n*-dodecane (70–100 μmol, internal standard) in solvent (3.0 mL) was distributed in 100 μL portions with a Pasteur pipette over 15–20 glass ampoules (i.d. = 3.0 mm). The ampoules were degassed and sealed by melting under N_2. They were heated in a constant-temperature (±0.5 °C) thermostat, taken out after defined intervals and quickly cooled. When all ampoules had been collected they were opened, transferred quantitatively to the sample containers of the autosampler and diluted with anhydrous toluene to a volume of 2.0 mL. Finally they were analyzed quantitatively by GC, to follow the kinetics, and by GC-MS for product identification. The results are recorded in the table. By-products typical of a radical mechanism were observed, generally in small yields, e.g. 1-phenoxytetralin and naphthalene (Table 1, entry 19) or 9-phenylxanthene (Table 1, entry 17).

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ESR: A solution (0.5 mL) of nitrobenzene (0.1 M) and xanthene (1.0 M) in diphenylether was transferred to an ESR sample tube, which was sealed by melting. It was heated to 269 °C and the spectrometer used under the following conditions: field centre: 3324.7 G; modulation: 0.63 G; microwave frequency: 9.3286 GHz; power: 15 dB. The spectrum is identical in all respects with one previously published [2].

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