The Surprisingly Facile Thermal Dehalogenation of Chlorinated Aromatics by a Hydroaromatic Donor Solvent. Tautomerization of Chlorinated Phenols and Anilines

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Up to 600 K, chlorinated benzenes and naphthalenes are inert in a hydrogen atom donating solvent such as 9,10-dihydroanthracene. However, when a hydroxyl or amine group is attached to the 2 or 4 position relative to chlorine, a surprisingly facile and selective hydrodehalogenation occurs at temperatures between 530 and 630 K. These features are the result of the onset of tautomeric equilibria for the chlorophenols or -anilines, creating the corresponding enones or imines, respectively, as reactive intermediates. The mechanism of dehalogenation involves the rate-determining transfer of a hydrogen atom from the solvent to the reactive intermediate according to a reverse radical disproportionation (RRD), followed by elimination of chlorine. The reactivity of mono- and dichlorophenols, chloroanilines, 4-chloro-1-naphthol, and 4-chloro-1-naphthylamine dissolved in 9,10-dihydroanthracene has been investigated. By means of density functional theory (DFT) calculations, the energies for the tautomers and their hydrogen affinities have been established. The experimental selectivities could be adequately reproduced by the computed data.

Introduction

The rigorous detoxification (dehalogenation) of waste streams containing aromatic organohalogen compounds, such as polychlorinated benzenes, phenols, and biphenyls, remains an area of continuing scientific interest. Gas-phase hydrodechlorination with molecular hydrogen at high temperatures has proven to be a viable approach next to the complete destruction by dioxygen in a controlled (catalytic) combustion.[1,2] Clear disadvantages, however, are that the high boiling and frequently not well-defined feed needs to be evaporated prior to chemical conversion, and that a flue gas treatment is required to ensure nonhazardous emissions. Alternatively, in the liquid phase and at elevated temperatures, hydrodesubstitution may occur when an aromatic compound is dissolved or suspended in a hydrogen-donating solvent. This methodology has been advanced to convert complex chemical (natural) matrices such as coal or lignin into easy-to-handle fluids.[3,4] One of the fundamental mechanisms underlying the reduction of the molecular weight involves a molecule−molecule reaction in which a hy-

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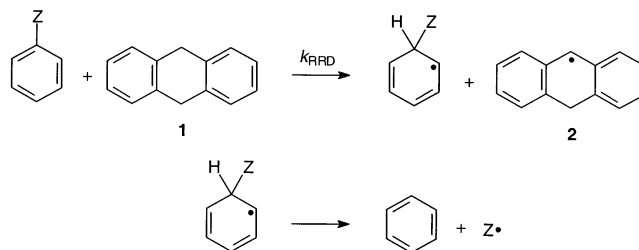
drogen atom is shuttled from the solvent to the target molecule, a process commonly referred to as reverse radical disproportionation (RRD).[5] Thus, when an aromatic compound carrying a substituent, Z, is dissolved in a donor solvent such as 9,10-dihydroanthracene (**1**), the RRD reaction creates two radical species, a cyclohexadienyl-type radical and 9,10-dihydroanthracenyl (**2**) (Scheme 1). Subsequent β-elimination of the Z radical leads to a regeneration of the aromatic system.

Provided that the second step is sufficiently fast, the overall rate of reaction is determined by the rate of the RRD for which the enthalpy of activation is about equal to the reaction enthalpy.[5,6]

Hydrodesubstitution of model compounds, 1-Z-naphthalenes with Z = F, Cl, Me, and OMe, by **1** sets in at around 630 K with a (standard) reaction time of 60 min.[7]

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(1) (a) Manion, J. A.; Mulder, P.; Louw, R. *Environ. Sci. Technol.* **1985**, *19*, 280−282. (b) Manion, J. A.; Louw, R. *J. Phys. Chem.* **1990**, *94*, 4127−4134. (c) Manion, J. A.; Louw, R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 551−557.

(2) (a) Brink, R. W.; Louw, R.; Mulder, P. *Appl. Catal. B* **1998**, *16*, 219−226. (b) Brink, R. W. Ph.D. Thesis, Leiden University, 1999.

(3) Dorrestijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder P. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 153−192 and references therein.

(4) Dorrestijn, E.; Kranenburg, M.; Poinsot, D.; Mulder, P. *Holzforschung* **1999**, *53*, 611−616 and references therein.

(5) Rüchardt, C.; Gerst, M.; Ebenhoch, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1406−1430 and references therein.

(6) Mulder, P.; Hemmink, S.; De Heer, M. I.; Lupo, M.; Santoro, D.; Korth, H. G. *J. Org. Chem.* **2001**, *66*, 6611−6619.

SCHEME 2
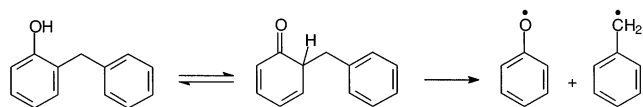
In preliminary experiments, we noted that under the aforementioned conditions the reduction of 4-chloro-1-naphthylamine into 1-naphthylamine was essentially complete, suggesting a dramatic change in reactivity or mechanism when replacing a hydrogen atom by a NH_2. From a thermokinetic perspective only a quite modest rate accelerating effect can be expected, since the reaction enthalpy for RRD is only marginally influenced by ring substitution.[5] Therefore, a rationale for the observation may be that the tautomeric imine, in equilibrium with the parent amine, acts as the relatively more reactive intermediate. Tautomerization has been shown earlier to be responsible for the facile thermal fragmentation of diphenylmethanes and diphenyl ethers with a hydroxyl group at the 2- or 4-position.[8] For example, ketonization of 2-hydroxydiphenylmethane yields a benzyl-substituted 2,4-cyclohexadienone intermediate (Scheme 2) with an intrinsically weak carbon–carbon bond, and subsequent homolytic cleavage results in the formation of a phenoxyl and a benzyl radical, which are turned into phenol and toluene, respectively, in the presence of **1**. The identical products would have been encountered when postulating a direct scission of the strong (aromatic) carbon–carbon bond in the starting material, but this pathway can be rejected since 3-hydroxydiphenylmethane is thermally stable under the applied conditions.

The decarboxylation of 4-hydroxybenzoic acid into phenol is complete at around 673 K when dissolved in a hydrogen donor solvent (tetralin) or a non-hydrogen donor solvent (naphthalene), while under the same conditions benzoic acid is inert.[9a] These features have been explained by proposing that the keto form of 4-hydroxybenzoic acid, formed after a 1,5-H shift, is the reactive intermediate. The subsequent decay is believed to proceed through an ionic mechanism (in a hydrocarbon solvent) involving the loss of a proton followed by decomposition into CO_2 and a phenoxyl anion.[9a,b]

These examples illustrate that tautomerization may be of importance in the thermal dehalogenation by hydrogen transfer for chloroaromatics containing an amine or a hydroxyl group. In this paper, we report on a mechanistic study pertaining to the reactivity of phenyl- and naphthyl-substituted compounds (Scheme 3) in 9,10-dihydroanthracene (**1**) as the hydrogen donor solvent. The energetics for tautomerization as well as the enthalpy of addition for a hydrogen atom to relevant (intermediate) species have been computed by density functional theory (DFT) method employing the B3LYP/6-31G(d,p) basis set to facilitate a thermokinetic rationale.

(7) (a) Arends, I. W. C. E.; Mulder, P. *Energy Fuels* **1996**, *10*, 235–242. (b) Arends, I. W. C. E. Ph.D. Thesis, Leiden University, 1993.

(8) McMillen, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322–3326.

(9) (a) Manion, J. A.; McMillen, D. F.; Malhotra, M. *Energy Fuels* **1996**, *10*, 776–788. (b) However, the decarboxylation might also occur by an electrophilic pathway via protonation of the aromatic ring by another molecule of benzoic acid: Eskay. T. P.; Britt, P. F.; Buchanan, A. C., III *Energy Fuels* **1997**, *11*, 1278–1287.

SCHEME 3
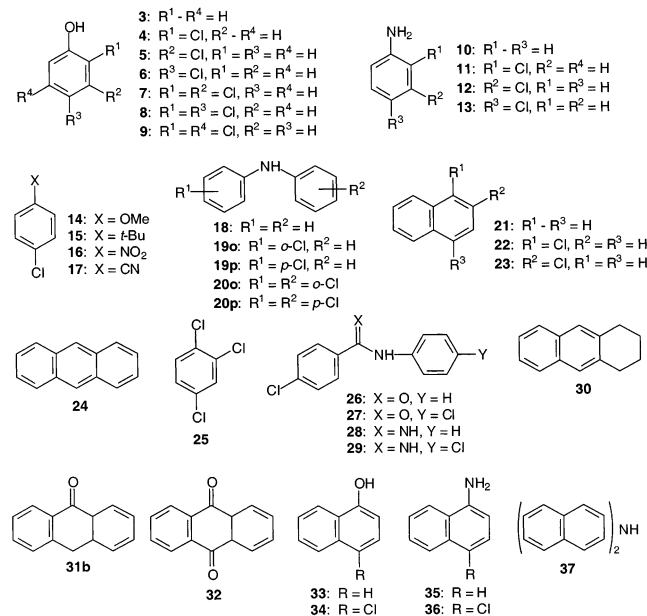
Results

Chlorophenols and Chloroanilines. The experiments were carried out in sealed Pyrex ampules. The reagent dissolved in the donor solvent 9,10-dihydroanthracene (**1**) with a molar ratio of [**1**]/[reagent] of about 3.7 was allowed to react for 3 h at 630 K. At the elevated reaction temperatures, partitioning of the compound of interest may occur between the liquid and the gas phase. To ensure that the reagent, i.e., the phenyl derivatives, remained in the liquid phase, the total vapor pressure inside the reaction vessel was fortified by adding a small amount of water.[10] We examined the reactivity of 2-chlorophenol (**4**), 3-chlorophenol (**5**), 4-chlorophenol (**6**), 2,3-dichlorophenol (**7**), 2,4-dichlorophenol (**8**), 2,5-dichlorophenol (**9**), 2-chloroaniline (**11**), 3-chloroaniline (**12**), 4-chloroaniline (**13**), 4-chloroanisole (**14**), 4-chloro-*tert*-butylbenzene (**15**), 4-chloronitrobenzene (**16**), and 4-chlorobenzonitrile (**17**). The results are summarized in Table 1.

At 523 K **6** was inert and the selective dechlorination to phenol (**3**) increased to 25% at 630 K, with the concomitant production of an equimolar amount of HCl. The conversion of **4** to **3** reached 74% at 630 K for 180 min, while **5** produced only minute amounts of **3** and HCl under these conditions. The three dichloro-substituted phenols (**7**–**9**) were investigated to corroborate the facile removal of chlorine at the 2- or 4-position relative to OH. An almost quantitative conversion of 2,3-dichlorophenol

(10) (a) The most volatile of the investigated substrates is **4** (bp 448 K). Its vapor pressure at the applied temperature (630 K) is 4.9 atm (ref 10b). Charging the reaction tube with 0.6 mmol of **4**, 2.2 mmol of **1** (bp 585 K), and 0.15 mmol of dibenzofuran (bp 560 K) (internal standard), leaves a headspace volume of 1.9 mL. Applying Raoult's law, approximately 30% of **4** would stay in the gas phase (decreasing to 14% with **6**, bp 493 K). By addition of typically 0.6 mmol of water (only in the case of phenyl derivatives)—corresponding to approximately 19 atm of overpressure under ideal gas approximation—virtually the entire substrate remains in the liquid phase. The substrate/water ratio was at least 1. Water was chosen because of the obvious advantage of not adding additional organic material to the reaction mixture. (b) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993.

TABLE 1. Hydrodechlorination of Chlorinated Phenols and Anilines (ClPhX) in 9,10-Dihydroanthracene (1) at 630 K^a

		yield (%)			$10^6 k_{exp}{}^b$
exp no.	ClPhX	ClPhX	HCl	PhX	(M^{-1} s^{-1})
1.1	2-ClPhOH (**4**)	26	74	74	51.5
1.2	3-ClPhOH (**5**)	99.7	1.8	0.3	≤0.1
1.3	4-ClPhOH (**6**)	75	25	25	8.6
1.4^c	4-ClPhOH (**6**)	78	11	4	
1.5	2,3-Cl$_2$PhOH (**7**)	1	103	99^d	208.8
1.6	2,4-Cl$_2$PhOH (**8**)	21	112	79^e	23.0/42.1^e
1.7	2,5-Cl$_2$PhOH (**9**)	38	61	62^d	33.3
1.8	2-ClPhNH$_2$ (**11**)	60	41	37^f	14.9^f
1.9	3-ClPhNH$_2$ (**12**)	99.6	1.5	0.4	≤0.1
1.10	4-ClPhNH$_2$ (**13**)	58	39	31^f	12.9^f
1.11^c	4-ClPhNH$_2$ (**13**)	0	92	37	
1.12^g	4-ClPhOMe (**14**)	99.5	1.5	0.5	≤0.2
1.12^g	4-ClPhtBu (**15**)	100		—^{h}	
1.13^g	4-ClPhNO$_2$ (**16**)	0	41	—^{i}	18.0^j
1.13^g	4-ClPhCN (**17**)	10		—^{i}	

^{a} With an initial ratio [**1**]/[reagent] of 3.66 ± 0.16 and a reaction time of 180 min. Recoveries for reactants and products were ca. 92–95%, as determined by blank runs. Hydrogen donor mass balance (**1**, **24**, and **30**) was 97–102%. Reported organic yields are based on a 100%-normalized mass balance, unless stated otherwise. The detection limit for organic products was ca. 0.3%; the purity of the reagents employed was higher than 98.5%. The HCl yield is given relative to the initial reagent concentration. ^{b} Experimental bimolecular rate constant computed from experimental pseudo-first-order disappearance of the starting material according to $\ln([ClPhX]/[ClPhX]_0) = -k_{exp}t[\mathbf{1}]_{av}$, using the average [**1**] between $t = 0$ and 180 min. ^{c} In biphenyl as the solvent, absolute yields. ^{d} **5** (3-ClPhOH) plus 0.3% phenol (**3**). ^{e} Sum of **4** (9%), **6** (40%), and **3** (30%). The overall k_{exp} is 6.51×10^{-5} M^{-1} s^{-1}. Two tautomers exist (**8a-2** and **8b**); removal of Cl yields **6** and **4**, respectively. Both products are subsequently partially dechlorinated to **3**. With the k_{exp} values for **6** and **4**, and the final product composition, the individual rate constants are approximated by an iterative method. ^{f} Next to aniline (**10**), the formation of diphenylamines **18**–**20** was observed with yields (in %), including a stoichiometric factor of 2: exp. no. 1.8, **18** (2.6), **19o** (0.7); exp. no. 1.10, **18** (2.6), **19p** (4.8), and **20p** (2.6). The k_{exp} value is obtained by first multiplying the global rate constant for disappearance by the product fraction: [**10**]/([**10**] + [**18**–**20**]). ^{g} For exps. 1.12 and 1.13 a 1:1 mixture of the reagents was used. ^{h} *tert*-Butylbenzene could not be detected as reaction product. ^{i} Absolute yields. The NO$_2$ group was completely reduced to NH$_2$, yielding **13** (44%) and **10** (17%). Two benzamides (see text and Scheme 3) were identified as well: **27** (26%) and **26** (13%). The HCl yield refers to [**16**]$_0$. Nitrobenzene and benzonitrile could not be detected as reaction products. Total recovery for nitrile derived compounds: 49%. ^{j} Assuming an instantaneous conversion of **16** into **13**.

(**7**) into 3-chlorophenol (**5**) occurred, whereas with 2,4-dichlorophenol (**8**) a product mixture consisting of **3**, **4**, and **6** emerged. 3-Chlorophenol (**5**) was the only product from 2,5-dichlorophenol (**9**).

The dechlorination pattern for chloroanilines appeared to be quite similar to that for chlorophenols. Aniline (**10**) was the main reaction product together with minor amounts of (chlorinated) diphenylamines **18**–**20** (Scheme 3) when reacting 2- and 4-chloroanilines (**11**, **13**), while 3-chloroaniline (**12**) showed hardly any reactivity. 4-Chloroanisole (**14**), i.e., replacement of the hydroxyl group in **6** by methoxyl, yielded only minute amounts of anisole, while under the same conditions 4-chloro-*tert*-butylbenzene (**15**) remained intact. It should be noted that the purity of the reagents used in this study was above 98.5% and small amounts of organic products or hydrochloric acid may well stem from nondisclosed impurities. The mass (organic and chlorine) balances were always better
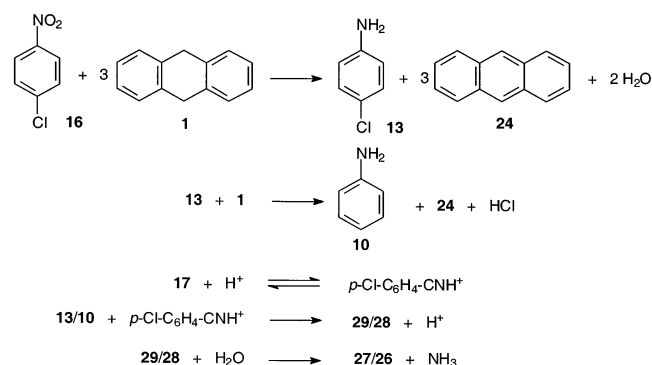
SCHEME 4
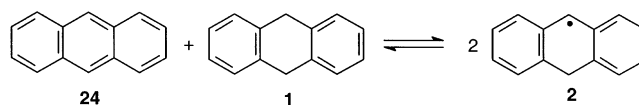
than 90%. In previous experiments with 1-chloro- (**22**) or 2-chloronaphthalene (**23**) in the presence of **1** and anthracene (**24**) at 610–680 K, we have established that the main chlorine elimination pathways are radical displacement by 9,10-dihydroanthracenyl (**2**) and condensation with **24**, both leading to the formation of 9-(naphthyl)anthracene derivatives.[7] The RRD reaction yielding naphthalene (**21**) is under these conditions only of minor importance.[7] The presence of **2** is dictated by the equilibrium, Scheme 4, which is firmly established at these temperatures. In contrast, with the phenyl derivatives used in this study the equivalent products, i.e., 9-(phenyl)anthracenes, could not be detected. The reactivity of 1,2,4-trichlorobenzene (**25**), dissolved in an equimolar mixture of **1** and **24** (with [**25**]/[**1**] = 1.4), was investigated with use of a prolonged reaction time of 900 min. This resulted in the formation of a dark-brown, sticky solution with low phenyl and anthracenyl mass balances (12 and 26%, respectively), suggesting a high degree of condensation; at the same time the absolute HCl yield (on reagent) was 59%. Product analysis revealed a molar ratio of **25**/dichlorobenzene/chlorobenzene = 1:1:0.05, with an ortho-, meta-, para-isomeric distribution for the dichlorobenzenes of 1:1.2:1.4. Traces of 9-(dichlorophenyl)anthracenes (three isomers) and pentachlorobiphenyls were found as well.

The intrinsic thermal stability of 4-chlorophenol (**6**) and 4-chloroaniline (**13**) was verified by replacing **1** by biphenyl as a non-hydrogen donor solvent, resulting in mixtures at 630 K with a high content of carbonaceous material and consequently poor organic mass balances. In these experiments the HCl production was lower (with **6**) or even higher (with **13**) when compared with the results obtained in **1**. In both cases, the amount of organic desubstitution product did not match the yield of HCl.

Quite interesting results were obtained with 4-chloronitrobenzene (**16**) in the presence of 4-chlorobenzonitrile (**17**) and dissolved in **1**. The nitro group in **16** was quantitatively reduced to **13**, followed by hydrodechlorination to **10** (Scheme 5).[11] The effective thermal reduction of a nitro group into an amine through RRD has been reported before. For example, nitrobenzene dissolved in an excess of **1** is quantitatively reduced to **10** at 553 K within 60 min.[5] This implies that at 630 K, **16** is reduced completely into **13** at an early stage of the reaction. Moreover, two benzamides, **26** and **27** (Scheme 3; Table 1), emerged as products from the reaction with **1**, most likely arising from hydrolysis of the corresponding benzamidines **28** and **29**, respectively, during the aqueous workup procedure. The benzamidine formation can be envisaged by protonation of the CN group of **17**, followed by addition of **10** or **13** to the corresponding nitrilium ion (Scheme 5). The mechanism is reminiscent of the acid-catalyzed addition of nucleophiles to benzonitriles,

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(11) The similar regioselective hydrogenation−dechlorination has been reported for 2,3-dichloronitrobenzene into **12** by Pd(PPh$_3$)$_4$: Angeloff, A.; Brunet, J.-J.; Legars, P.; Neibecker, D.; Souyri, D. *Tetrahedron Lett.* **2001**, *42*, 2301−2303.

SCHEME 5

indicating that ionic reactions can be of importance even in a nonpolar environment.[12] The ratio between the two benzamides **26** and **27** ([**27**]/[**26**] = 2.0) is quite comparable to that between the anilines **13** and **10** ([**13**]/[**10**] = 2.6), in accordance with Scheme 5.

An equivalent amount of anthracene (**24**) will be formed next to HCl in the hydrodechlorination by **1** through RRD of chlorinated aromatics. In addition, the independent self-hydrogenation of **1** results in an equivalent mixture of **24** and 1,2,3,4-tetrahydroanthracene (**30**). In most cases, even carefully purified **1** contains some **24** (ca. 1%), 9-anthrone (**31b**) (ca. 1%), and 9,10-anthraquinone (**32**) (ca. 0.5%) as impurities, resulting from the inadvertent interaction of molecular oxygen with **1** at ambient temperatures. Blank runs with **1** at 630 K showed the formation of an excess of **24** relative to **30** due to the (partial) reduction of the ketones **31b** and **32**, to reach a [**1**]/[**24**]/[**30**] ratio of 0.94:0.05:0.01 after 3 h.[6] Similar results were obtained in the presence of compounds **5**, **12**, **14**, and **15**, underscoring their low (if any) reactivity. In the presence of the other (reactive) phenols and anilines (**4**, **6**−**9**, **11**, **13**), the anthracene formation depended on the degree of conversion of the reagent. The dechlorination of the in situ formed **13** from **16** was 28%, somewhat different from experiments starting directly with **13** (39%). This variation can be attributed to the lower hydrogen donor concentration resulting from the reduction of the NO_2 group in **16**. With an intake [**1**]/[**16**] ratio of 1:0.27, the distribution of the anthracene moieties of [**1**]/[**24**]/[**30**] was 0.06:0.92:0.02 after reaction, showing that the hydrogen donor had been consumed almost entirely as a result of the quantitative reduction of the nitro group in **16** ($RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$) requiring 3 × 0.27 = 0.81 equiv of **1** (see Scheme 5).

On the basis of the pseudo-first-order rate of disappearance of the starting compounds, the experimental bimolecular rate constant, k_{exp}, for hydrodechlorination can be estimated by using the equation $\ln([ClPhX]/[ClPhX]_0) = -k_{exp}t[\mathbf{1}]_{av}$, with $[\mathbf{1}]_{av}$ as the average hydrogen donor concentration between $t = 0$ and 180 min. Rate constants obtained in this way are collected in Table 1, showing that the presence of a hydroxyl or amino group at the 2- or 4-position effectively accelerates the rate of hydrodechlorination for chlorinated phenyl compounds by at least a factor of 100 at 630 K.

Substituted Naphthalenes. The rate of desubstitution of 4-chloro-1-naphthol (**34**) into 1-naphthol (**33**) by

(12) Smyth, R. M.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2171−2174.

TABLE 2. The Effect of Initial Concentration and of Various Additives on the Dechlorination of 4-Chloro-1-naphthylamine (36) in 9,10-Dihydroanthracene (1) at 523 K[a]

exp. no.	ratio [**1**]/[**36**][b]	yield (%)		
		36	**35**	**HCl**
2.1	5	13	66[c]	85
2.2	8	39	52[c]	59
2.3	20	51	49	50
2.4	39	45	55	56
2.5	81	49	51	54
2.6	162	79	21	26
2.7	284	88	12	10
2.8	492	90	10	−[d]
2.9[e]	33	100	0	0
2.10[f]	287	94	6	5
2.11[f]	324	66	34	−[g]
2.12[f]	29	27[h]	−[i]	73

[a] With a reaction time of 72 min. Recoveries for reactant and product 1-naphthylamine (**35**), as determined by blank runs, were 97−99%. Solvent mass balance (**1** and **24**) was 97−102%. Reported organic yields are based on a 100%-normalized mass balance, unless stated otherwise. The inorganic (HCl) yield relates to [**36**]$_0$. [b] Initial ratio. [c] Additional dinaphthylamine (**37**) formation, including a stoichiometric factor of 2: exp. no. 2.1, 21%; exp. no. 2.2, 9%. [d] Below detection level. [e] In biphenyl solution. [f] In the presence of additives, with [additive]/[**36**] = 7. Additives: exp. no. 2.10, quinoline; exp. no. 2.11, *p*-toluenesulfonic acid monohydrate; exp. no. 2.12, **35**. [g] Not determined. [h] Relative to [**36**]$_0$. [i] A 26% yield of **37** (relative to added **35**) was found.

1 was already appreciable (about 19%, see below) at much lower temperatures, i.e., at 523 K compared to 630 K for **6** at 1 h reaction time. The experimental reproducibility, however, was not satisfying. One of the reasons was the incompatible extraction procedure used for the chloride determination. When the acidity of a standard solution composed of **33**, **34**, and KCl at room temperature was rapidly increased by addition of concentrated HNO_3 (see the Experimental Section), the formation of a black precipitate was observed. Following the extraction protocol, the recoveries of the organic compounds and inorganic Cl were 1% and 100%, respectively. When the mixtures of the (chlorinated) phenols were treated the same way, the recoveries were always higher than 95%. Most likely, naphthol derivatives suffer from an acid-catalyzed oligomerization already manifest at ambient temperatures.[13] Some improvement could be achieved by more careful (slower) acidification and working with more dilute reaction mixtures. To serve as an indication, the dechlorination of **34** in **1** at 523 K and a reaction time of 60 min is about 19%. Under the same conditions, the dehalogenation of 4-chloro-1-naphthylamine (**36**) in **1** at 523 K resulted in the formation of 1-naphthylamine (**35**), HCl, and **24** in equimolar amounts. At these temperatures self-hydrogenation of **1** does not occur. In a biphenyl solution at 523 K **36** was found to be completely stable. The effect of the initial concentration was explored at constant [**1**]$_0$ by partially replacing **36** by biphenyl to achieve a range for the [**1**]/[**36**] ratio of 500 to 5. The results are collected in Table 2. The dehalogenation rate

(13) A comparable observation has been reported for the self-decomposition of 2-chloro-4-methoxy-1-naphthol. At room temperature and in the presence of an acid, this compound dimerizes within a few hours with loss of chloride and methoxyl into a mono-chloronaphthofuran derivative. Isomers with the Cl at the C-3 position are stable: Laatsch, H. *Liebigs Ann. Chem.* **1991**, 385−386.

TABLE 3. B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)-Calculated $\Delta_t G$ and $\Delta_t H$ Values for Tautomerization[a] and the Hydrogen Affinity, HA,[b] for Enones and Imines (in kcal mol^{-1} at 298 K)

parent compd	tautomer	$\Delta_t G$	$\Delta_t H$	HA	parent compd	tautomer	$\Delta_t G$	$\Delta_t H$	HA
3	**3a**	16.2	17.0	−44.1[c]	**10**	**10a**[e]	27.4	28.1	−55.5
	3b	15.8	16.1	−40.5		**10b**	25.7	25.8	−50.9
4[d]	**4a-2**	22.8	23.7	−58.8	**11**[d]	**11a-2**	31.0	31.7	−70.1
	4a-6	18.5	19.5	−47.0		**11a-6** [f]	28.1	28.9	−56.9
	4b	18.2	18.7	−43.6		**11b**[f]	26.5	26.7	−52.1
6	**6a**	16.8	17.6	−45.3[c]	**13**	**13a**	27.8	28.6	−56.6
	6b	18.9	19.4	−54.5		**13b**[e]	27.6	27.8	−65.7
7[d]	**7a-2**	20.8	21.6	−58.1	**18**	**18a**	24.9	25.5	−53.3
	7a-6	17.5	18.4	−46.5		**18b**	23.0	22.9	−49.5
	7b	16.7	17.2	−44.0					
8[d]	**8a-2**	23.0	23.8	−58.3	**35**	**35a** [g]	16.9	17.7	−47.5
	8a-6	18.9	19.9	−48.0		**35b**	16.5	16.9	−50.1
	8b	21.2	21.8	−56.3	**36**	**36a**[g]	17.6	18.2	−48.6
9[d]	**9a-2**	22.1	23.0	−58.3		**36b**	17.7	18.2	−59.5
	9a-6	17.4	18.3	−47.0	**37**	**37a**	12.7	13.6	−48.5
	9b	17.1	17.6	−44.3		**37b**	12.4	12.6	−48.5
33	**33a**	6.2	6.9	−35.2	**39**	**39b**	5.6	5.7	−50.7
	33b	6.7	7.2	−39.3	**40**	**40b**	4.8	5.0	−49.6
34	**34a**	6.6	7.4	−35.8					
	34b	8.9	9.5	−48.4					
31	**31b**	−6.1	−6.6	−36.9					
38	**38b**	−6.1	−5.9	−47.3					

[a] $\Delta_t G$ and $\Delta_t H$ are defined as the difference in energy between the parent aromatic compound and its tautomer, e.g. **3** → **3a**, both in the lowest energy conformation. [b] The hydrogen affinity (HA) is defined as the heat of reaction, $\Delta_r H(R + H^\bullet \rightarrow RH^\bullet)_{298}$, of addition of a hydrogen atom to exocyclic oxygen or nitrogen of the tautomer in the lowest energy conformation. The index **a** and **b** denotes the tautomeric structure (see Scheme 6), the second number refers to the position of the methylene group (CHCl, CH$_2$). [c] For **3a** and **6a**, and with the OH oriented cis relative to CH$_2$ in the radicals, the HAs are −42.8 and −44.0 kcal mol^{-1}, respectively. [d] The lowest energy conformer for the aromatic compound with a Cl at C-2 contains an intramolecular hydrogen bond, and the hydrogen bond energy or enthalpy, $\Delta_{intraHB}G$ or $\Delta_{intraHB}H$, is defined as the energy difference between the OH in the toward and the away orientation. For the phenols **4**, **7**, **8**, and **9** the $\Delta_{intraHB}G$ is −3.0, and the $\Delta_{intraHB}H$ is −3.1 kcal mol^{-1}; the non-hydrogen-bonded species for **11** does not exist. [e] The $\Delta_t G$ ($\Delta_t H$) is independent of the orientation of the NH group (i.e. toward or away to CHCl or CH$_2$) for the imines **11a-2**, **13a**, and **18a**. [f] The $\Delta_{intraHB}G$ and $\Delta_{intraHB}H$ for **11a-6** are − 1.2 and − 2.0, and for **11b** − 2.0 and − 2.0 kcal mol^{-1}, respectively. [g] With the NH group trans to CH$_2$, $\Delta_t G$ and $\Delta_t H$ are 18.9 and 19.1 kcal mol^{-1} for **2a** and 18.4 and 18.7 kcal mol^{-1} for **3a**.

increased as the concentration ratio, [**1**]/[**36**], decreased and reached a plateau value of about 50% at [**1**]/[**36**] = 80−20. For more concentrated solutions, i.e., [**1**]/[**36**] = 5, the dehalogenation increased to ca. 87%. Under these conditions, 1,1′-dinaphthylamine (**37**) emerged as an additional reaction product with a yield of 21% (considering a stoichiometric factor of 2). We were not able to detect possible chloro-substituted dinaphthylamines, even when the concentrations of parent amines **35** and **36** were about equal (see Table 2, exp. no. 2.2). When a 7-fold excess (relative to **36**) of the reaction product 1-naphthylamine (**35**) was added to the starting mixture at a [**1**]/[**36**] ratio of 30, the conversion increased from 50% to 73%, together with a considerable formation of **37**. It was verified that in the absence of acidic species **35** was thermally stable up to 663 K in 9,10-dihydroanthracene solution. The involvement of acid catalysis was substantiated by the addition of an organic base as an acid trap or an organic acid to the reaction mixture under conditions of high initial dilution of **36**. Addition of an excess of quinoline somewhat slowed the rate of conversion, while *p*-toluenesulfonic acid effectively accelerated the hydrodechlorination (see Table 2, exp nos. 2.10 and 2.11).

At higher temperatures, **36** was reacted in competition experiments with 1-chloronaphthalene (**22**) or 2-chloronaphthalene (**23**) dissolved in a 1:1 mixture of **1** and **24**. At 617 K and a reaction time of 68 min, **36** was converted for >99.9%, **22** for 14%, and **23** for about 4%. Similar to lower reaction temperature conditions, **36** yielded selectively **35** and **37**. With **22** or **23**, the selectivity toward the product of hydrodechlorination, naphthalene (**21**), was 10% for **22** and 41% for **23**, respectively. In both

SCHEME 6
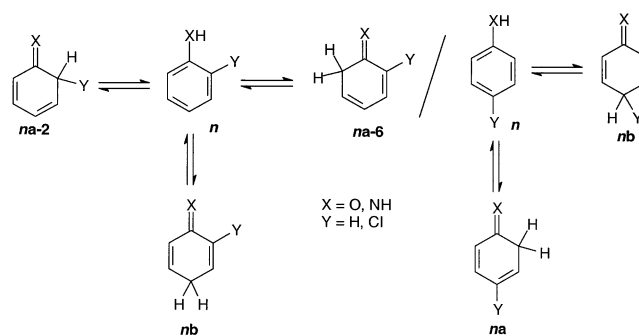
cases the formation of 9-(naphthyl)anthracenes predominated. Possible anthracene-coupling products with **36** could not be detected, indicating the presence of a different reaction channel for hydrodechlorination.

Energetics for Tautomerization. The experimental findings strongly suggest that not the parent phenols or anilines but rather the corresponding enones and imines act as the reactive intermediates. Experimental data regarding the energetics for tautomerisation of OH- and NH$_2$-substituted aromatics are scarce. We have used the popular B3LYP DFT methodology with the 6-31G(d,p) basis set to compute the energies of a series of phenyl, naphthyl, and anthracenyl derivatives to obtain an internally consistent set of thermodynamic data. The computed Gibbs energies, $\Delta_t G$, and enthalpies, $\Delta_t H$, for tautomerization are presented in Table 3. As indicated in Scheme 6, the 1,2- and 1,4-tautomers of the aromatic alcohols or amines are denoted by adding **a** or **b** to the
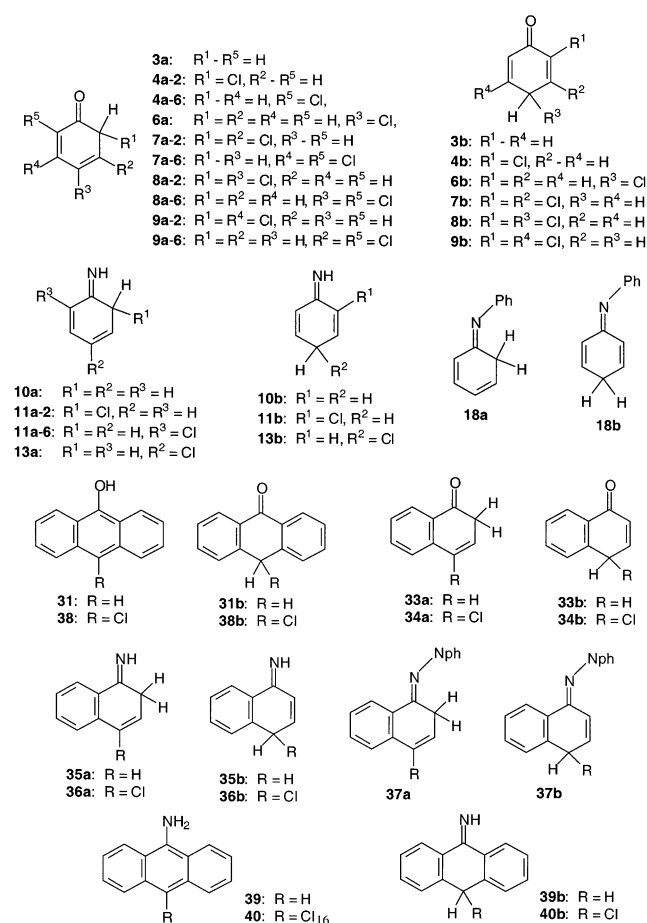
SCHEME 7

TABLE 4. The Heats of Formation, $\Delta_f H_{298}$, for ArXH (X = O, N) and Their Tautomeric Entities a and b[a]

ArXH	$\Delta_f H_{298}$[b] ArXH[c]	a	b
3[c]	−23.0	−6.0	−6.9
33	−6.7	0.2	0.5
31	13.9		7.3[d]
10[c]	20.8	48.9	46.6
35	38.2	55.9	55.1
39	59.0		64.6

[a] In kcal mol^{−1}; **a** or **b** refers to the position of the methylene group in the tautomer, see Scheme 6 and 7. [b] $\Delta_f H_{298}$ for **a** or **b** is computed by using the $\Delta_t H$ from Table 3, combined with auxiliary thermodynamic data from ref 14. [c] See ref 14. [d] The average experimental $\Delta_f H_{298}$ for 9-anthrone (**31b**) is 5.9 kcal mol^{−1} (see ref 14).

number of the parent aromatic compound, the number for the 1,2-tautomer supplemented by -**2** or -**6** to identify the position of the sp[3] carbon atom (CHCl or CH₂ group) in cases where two regioisomers are possible. The structures are displayed in Scheme 7.

From the data of Table 3 it can be inferred that the entropy changes associated with tautomerization are quite modest, that is, DFT predicts a $\Delta_t S$ of about 3 cal mol^{−1} K^{−1} at most.

In Table 4, we have collected the heats of formation, $\Delta_f H_{298}$, for some prototypical tautomeric entities using the information from Table 3 combined with auxiliary thermodynamic data.[14] The $\Delta_f H$ values for the tautomers

SCHEME 8
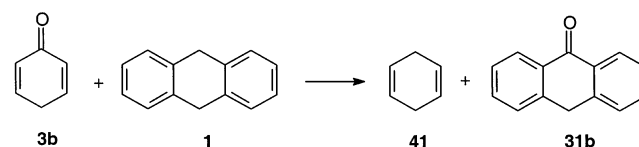
3a and **3b** of phenol have been determined by using a flowing afterglow technique as −17 ± 3 and −13 ± 3 kcal mol^{−1}, respectively.[15] These values deviate substantially from our computed ones of −6.0 and −6.9 kcal mol^{−1} (Table 4). From experience, it appears highly unlikely that such a large deviation can be attributed to an erroneous handling by DFT of the compounds under investigation, in particular because in the computations of the energetics for tautomerization, the number of molecules remains constant, providing the advantage of the cancellation of computational errors. This view is supported by the fact that for 9-anthrone (**31b**), the difference between computed and experimental $\Delta_f H$ is only 1.4 kcal mol^{−1}, see Table 4.

An alternative way to asses the $\Delta_f H_{298}$ values for the tautomers **3b** of phenol and **33b** of 1-naphthol is to apply an isodesmic reaction, such as shown in Scheme 8, and combine the DFT-computed $\Delta_r H$ values with (experimental) literature data for the other species.[14]

The changes in the $\Delta_f H$ for **3b** and **31b** (see Table 4) remain within a reasonable (computational) error margin of about 0.5 kcal mol^{−1}. Therefore, it can be concluded that the reported experimental $\Delta_f H$ values for the tautomeric forms of phenol are most likely in error.[15] It has been firmly established that for the 9-anthrol/9-anthrone system, the keto form, **31b**, is energetically the more stable species in a non-hydrogen bonding solvent. Experimentally, the equilibrium constant in cyclohexane[16] at 298 K has been determined as 10[3], or $\Delta_t G$ = −4.1 kcal mol^{−1}, which deviates somewhat from the free energy change predicted by DFT of −6.1 kcal mol^{−1} (see Table 3). Further inspection of Table 3 reveals that $\Delta_t H$ depends on the position of the chlorine substituent. For example, when comparing the $\Delta_t H$ values for **6b** and **3b**, the change in $\Delta_t H$ of 3.3 kcal mol^{−1} can be fully associated

(14) (a) The auxiliary heats of formation, $\Delta_f H$, in kcal mol^{−1}, at 298 K used in this study are taken from ref 14b, unless stated otherwise; $\Delta_f H$(**31b**) = 5.88 (average of 5.04, ref 14c; 5.59, ref 14b; 7.0 ref 14d); $\Delta_f H$(1,2-dihydronaphthalene) = $\Delta_f H$(1,4-dihydronaphthalene) = 32.0 from ref 14e, combined with the recommended $\Delta_f H$(1,4-cyclohexadiene) from ref 14b; $\Delta_f H$(**1**) = 38.2 from ref 14e. DFT estimates for the isodesmic reaction phenol + naphthalene → benzene + 1-naphthol a $\Delta_r H_{298}$ of 0.0, and combined with the tabulated $\Delta_f H$ values for the other species provides $\Delta_f H$(**33**) = −6.73 (according to ref 14b: −7.25); for phenol + anthracene → benzene + 9-anthrol with a $\Delta_r H_{298}$ of 1.55, gives $\Delta_f H$(**31**) = 13.92. For aniline + naphthalene → benzene + 1-naphthylamine, DFT predicts a $\Delta_r H_{298}$ of 1.07, leading to $\Delta_f H$(**35**) = 38.17 (according to ref 14b: 38.0), and aniline + anthracene → benzene + 9-aminoanthracene together with $\Delta_r H_{298}$ of 2.76 leads to $\Delta_f H$(**39**) = 58.96. (b) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom P. J., Mallard, W. G., Eds; July 2001; National Institute of Standards and Technology, Gaithersburg MD, 2001 (http://webbook.nist.gov). (c) Verevkin, S. P. *Thermochim. Acta* **1998**, *310*, 229−235. (d) Stein, S. E.; Rukkers, J. M.; Brown, R. L. *NIST Structures and Properties Database 25*, version 2.0; NIST Standard Reference Data; National Institute of Standards and Technology: Gaithersburg, MD, 1994. (e) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 1716−1729.
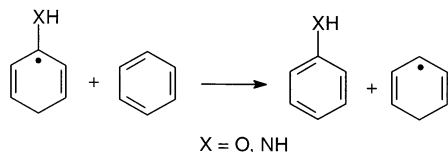(15) Shiner, C. S.; Vorndam, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 5699−5701.
(16) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216−1224.

SCHEME 9
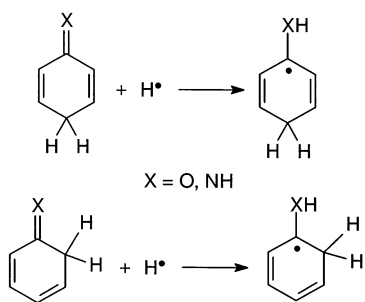
SCHEME 10

with the weaker carbon−hydrogen bond formed in tautomer **6b**, due to the presence of the chlorine at that carbon atom, while at the same time the BDE(O−H) values for **6** and **3** are about the same.[17] The $\Delta_t H$ for **4** (and other 2-chloro-substituted compounds) varies depending on the conformation of the parent phenol. The lowest energy conformer of **4** possesses an intramolecular hydrogen bond between the hydroxylic hydrogen and chlorine. Upon tautomerization, this hydrogen bond needs to be ruptured and as a consequence the $\Delta_t H$ increases.[18]

Hydrogen Affinities of the Tautomers. The dynamics for RRD is governed by the reaction enthalpy for hydrogen atom transfer. Therefore, the hydrogen affinities (HA) of the tautomers under study, defined as the heat of addition, $\Delta_r H(S + H^\bullet \rightarrow SH^\bullet)$, of a hydrogen atom to the exocyclic C=X double bond (Scheme 9), have been calculated by DFT and are summarized in Table 3. Another way to predict the HA (and to diminish possible computational errors) is starting with an isodesmic reaction such as shown in Scheme 10.

Combination of the $\Delta_r H$ values computed by DFT and auxiliary thermodynamic data allows the calculation of the $\Delta_f H$ values for the corresponding adduct radicals.[19,20] Subsequently, it furnishes the HA values for the ketones and imines when using the thermodynamic data provided by Table 4. The scaled HA values calculated in this way are compiled in Table 5. A comparison with those computed directly by DFT shows that the largest deviation (overestimation) occurs for monocyclic compounds. With the thermodynamic data for the adduct radicals, the HA values for the parent aromatic alcohols and amines can be derived as well. From Table 5, it can be seen that the HA values for the addition of a hydrogen atom at C-4 (or C-9) for these compounds are in good agreement with those advanced as experimental HA

TABLE 5. DFT-Scaled Hydrogen Affinities (HA) for Aromatic Alcohols and Amines and Their Tautomers, and Allylic/Benzylic BDE(C−H) Values in the Enones and Imines[a]

	HA[b]	BDE(C−H)[c]		HA[b]	BDE(C−H)[c]
3	−24.4/−21.7	*87.2*[d]	**10**	−24.6/−22.4	*89.7*[d]
3a	−41.4 (−44.1)	70.2	**10a**	−52.7 (−55.5)	61.6
3b	−37.8 (−40.5)	71.1	**10b**	−48.2 (−50.9)	63.9
33	−27.0/−31.1	*81.0*[d]	**35**	−28.9/−32.2	*85.0*[d]
33a	−33.9 (−35.2)	74.1	**35a**	−46.6 (−47.5)	67.3
33b	−38.3 (−39.3)	73.8	**35b**	−49.1 (−50.1)	68.1
31	−44.8	*69.8*[d]	**39**	−46.3	*78.5*[d]
31b	−38.2 (−36.9)	76.4	**39b**	−52.0 (−50.7)	72.8

[a] In kcal mol⁻¹, at 298 K. See also footnote *a* in Table 3. [b] The scaled HA values are obtained by means of an isodesmic reaction, see Scheme 10, in combination with auxiliary thermodynamic data (see Table 4, and refs 14, 19, and 20). In parentheses is presented the HA value as computed by DFT directly (see Table 3). The HA for the aryl compounds refers to addition of a hydrogen atom to C-2/C-4 (**3**, **33**, and **10**, **35**) or C-10 (**31**, **39**). [c] For example, the BDE(C−H) in the enone **3b** is derived by using the thermodynamics for the equation **3b** → PhO• + H• ← **3**, together with the scaled DFT BDE(O−H) as presented in this table, and the heat of tautomerization as given in Table 3. [d] The values in italics are the BDE(O−H) values and BDE(N−H) values for the aryl compounds, see ref 21.

values for the unsubstituted aromatics.[20] Finally, the BDE(C−H) values for the enones and imine are extracted from the data by using equations such as **3b** → PhO• + H• ← **3** in combination with $\Delta_f H$ values from Table 4, and the scaled DFT BDE(X−H) values for X = N, and O.[21] Interestingly, the BDE(C−H) for the enones increases from 71.1 (**3b**) to 76.4 (**31b**) kcal mol⁻¹; the former is lower, about 6 kcal mol⁻¹, when compared with 1,4-cyclohexadiene, while the later is almost identical to BDE(C−H) in 9,10-dihydroanthracene.[20] This feature is related to a relative reduction of the stabilization enthalpy for the incipient oxyl radicals when starting from the enone. Indeed, DFT predicts that the (Mulliken) spin density on oxygen decreases from 0.445 (phenoxyl) to 0.182 (anthroxyl). For the same reason the BDE(O−H) for the aromatic alcohols decreases in the series **3**, **33**, and **31**; removal of the phenolic hydrogen from **31** yields a more stabilized radical species. Table 5 demonstrates that enones and imines possess weakly bonded hydrogens, which implies that these compounds can be readily oxidized by dioxygen even at ambient temperatures.

Some other key features can be noted from the HA data presented in Table 3. Formation of an intramolecular OH−Cl hydrogen bond is largely responsible for the difference in HA between **3a** and **4a**−**6**.

(17) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090−4092.

(18) Korth. H.-G.; de Heer, M. I.; Mulder, P. *J. Phys. Chem. A* **2002**, 106, 8779−8789.

(19) DFT computes, in kcal mol⁻¹, for Scheme 10, with the tautomeric precursor for the adduct radicals in parentheses, a $\Delta_r H$ of 2.40 (**3a**), −0.34 (**3b**), 0.70 (**33a**), −0.20 (**33b**), 0.64 (**31b**), 2.60 (**10a**), 0.40 (**10b**), 2.60 (**35a**), 0.90 (**35b**), and 2.10 (**39b**).
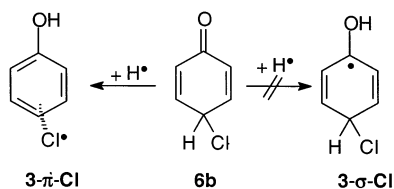
(20) (a) The assumption is that the experimental allylic/benzylic BDE(C−H) values in the hydroaromatics 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene are identical, i.e., 77 kcal mol⁻¹(refs 14b and 20b), and that BDE(C₁−H) in 1,2-dihydronaphthalene is 82 kcal mol⁻¹, using the experimental BDE(C−H) for toluene as the reference (ref 6). Removal of the allylic/benzylic hydrogen from the hydroaromatic affords a radical identical with the one for addition of a hydrogen atom to the fully aromatic compound, and the derived HAs are 22.0 (benzene), 31.3 (naphthalene, C-1), 26.3 (naphthalene, C-2) and 44.2 (anthracene, C-9). According to DFT, the BDE(C−H) values within the series of hydroaromatics 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and 9,10-dihydroanthracene are 72.3, 72.2, 72.9, 81.0, and 75.2 kcal mol⁻¹, giving HAs of 24.7, 24.7, 32.4, 27.7, and 42.9 kcal mol⁻¹, respectively (data from ref 6, except for 1,3-cyclohexadiene, 1,4-cyclohexadiene). Thus DFT, for example, underestimates the BDE(C−H) in 1,4-cyclohexadiene and overestimates the HA for benzene suggesting an erroneous computational handling of the radical and the diene. (b) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152−1155.

SCHEME 11

When comparing **3b** (without chlorine) and **6b** (with chlorine), the computed HA decreases from −40.5 to −54.5 kcal mol⁻¹. However, the DFT calculation predicts for the **6b** + H· reaction as a lowest energy product not the cyclohexadienyl radical **3**-σ-**Cl** but rather a chlorine−arene π-complex **3**-π-**Cl** (Scheme 11) with a chlorine−arene distance of about 2.5 Å. A similar situation holds for all 2- and 4-chloro-substituted tautomers. The difference in $\Delta_f H$ between the π and σ chlorine−benzene radical adduct has been estimated to be around 7 kcal mol⁻¹ in favor of the σ species.[22] Apparently, DFT identifies a post-transition-state complex as the lowest energy ensemble, stabilized by π-type interaction (and additional hydrogen bonding between Cl and the adjacent hydroxyl or amine group for the 2-chloro-substituted systems).[23] Although obscured by this characteristic of the DFT method, the HA values for the enones **a**-**2** of all 2-substituted phenols studied are almost invariant (**4**, −58.8 kcal mol⁻¹; **7**, −58.1 kcal mol⁻¹; **8**, −58.3 kcal mol⁻¹; **9**, −58.3 kcal mol⁻¹). Furthermore, the change in HA between **4a**-**2** and **6b** is about the same as for the two tautomers **3a**, **3b** of phenol. Similar to the chlorinated phenols and anilines, the computed HA values for the carbon carrying the chlorine in 1-chloro- and 2-chloronaphthalene (**22**, **23**) refer to π-complexes, with the chlorine atom interacting preferably with C-1. Thus, for

23 the lowest energy structure of the hydrogen atom adduct appears to be a π-complex with the chlorine atom having shifted from C-2 in the parent compound to C-1 in the complex. The corresponding HA values are −35.0 kcal mol⁻¹ for **22** and −34.5 kcal mol⁻¹ for **23**, suggesting an almost identical reactivity of both isomers, in clear contrast with the HA values of −31.3 and −26.3 kcal mol⁻¹ for C-1 and C-2 in naphthalene.[20]

Discussion

The foregoing results show that chlorines attached to the 2- or 4-position in aromatic alcohols or amines, e.g. phenols or anilines, can be removed with a remarkably high selectivity in the presence of hydrogen donor solvents such as 9,10-dihydroanthracene (**1**). Under similar conditions elimination of Cl at C-3 does not occur. At elevated temperatures and in the presence of **1** and (in situ formed) anthracene (**24**) an appreciable stationary concentration of the 9,10-dihydroanthracenyl radical (**2**) is present in the reaction mixture (see Scheme 4).[7] Since, in principle, the thermal decomposition of **2** may act as a source for hydrogen atoms, it might be postulated that these species are responsible for the observed hydrodechlorination. Earlier, it has been demonstrated that in the gas phase and at around 1000 K, the hydrodechlorination rate for chlorophenols by an addition/elimination mechanism is exclusively governed by the rate of the addition of the hydrogen atom. Relative rates for **4**, **5**, and **6** have been established as 1.6:1:1.5.[1b] This hydrogen atom chemistry leads to the elimination of other substituents as well. According to gas-phase kinetic parameters, the relative rates for hydrodesubstitution of chlorobenzene, phenol, and aniline are quite comparable (1:0.3:0.4 at 630 K).[24] In the present study, however, chlorobenzene from chlorophenols and chloroanilines or 1-chloronaphthalene (**22**) from **36** was never observed as a product. Therefore, it can be concluded that free hydrogen atom chemistry is not of any importance for the present liquid phase reaction conditions and that RRD is most likely the ruling mechanism. The rate of dechlorination of the chloroaromatics is dramatically increased as a result of the introduction of an OH or NH₂ group. Besides, the product distribution is quite different. From, e.g., 4-chloro-1-naphthylamine (**36**) only 1-naphthylamine (**35**) is found, whereas with 1-chloronaphthalene (**22**) the formation of an array of condensation products predominates. All these findings indicate that tautomerization prior to RRD plays a pivotal role in the hydrodesubstitution mechanism for a defined category of aromatic compounds. In the following sections we will discuss some dynamic aspects.

Hydrodechlorination: Relative Rates. A general expression has been developed for the rate constant for RRD, k_{RRD}, and requires only the knowledge of the reaction enthalpy, $\Delta_{RRD}H$ (eq 1), with $\ln(A_{RRD}) = 13.6 +$

$$k_{RRD} = A_{RRD} \exp[-(\Delta_{RRD}H + 3)/RT] \qquad (1)$$

$0.16\Delta_{RRD}H$, and $\Delta_{RRD}H$ in kcal mol⁻¹.[6] This equation predicts that when the hydrogen transfer becomes less

(21) (a) The bond dissociation enthalpies (BDE) of the O−H and N−H bonds for the parent compounds have been computed as well by our DFT method, and they are presented in Table 5 as scaled BDEs, using the experimental values for the BDE(O−H) in phenol and the BDE(N−H) in aniline as references. Although the BDE(O−H) in **3**, which is experimentally determined as 87.2 kcal mol⁻¹ (ref 21b), is underestimated by DFT at this level of theory by about 4 kcal mol⁻¹, the computed change in BDE(O−H), ΔBDE(O−H), upon substitution, is quite independent of the methodology applied and agrees with the experiment (ref 21c). This is reinforced by the present work: the experimental and DFT-computed ΔBDE(O−H) values for 1-naphthol (**33**) are almost identical (−5.9 versus −6.2 kcal mol⁻¹) (ref 21d). For **10** DFT predicts a BDE(N−H) of 87.9, which is 2 kcal mol⁻¹ below the best experimental value (ref 21e). As for the phenols, it may be assumed that the ΔBDE(N−H) values for the aromatic amines are sufficiently reliable (ref 21f). The change in BDE(O−H) or BDE(N−H) in phenyl derivatives upon ring substitution can be mainly attributed to the degree of delocalization of the unpaired electron in the corresponding phenoxyl and anilinyl radicals (refs 20c and 20f). This also appears to be valid when expanding the aromatic system from phenyl to anthracenyl. The effect is more profound for O−H than for N−H bonds, because of the higher intrinsic spin delocalization in aromatic oxyl than in aminyl radicals. (b) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737−8744. (c) Pratt, D. E.; De Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518−5526. (d) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736−1743. (e) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1997**, *62*, 3413−3414. (f) Pratt, D. A.; Dilabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085−11092.

(22) Benson, S. W. *J. Am. Chem. Soc.* **1993**, *115*, 6969−6974.

(23) At this level of theory we noted a similar deviation for the hydrogen abstraction by an alkoxyl radical from phenol, RO· + PhOH → ROH + PhO·, DFT assigns a hydrogen bonded post transition-state complex as the lowest energy product instead of the two separated species: De Heer, M. I.; Mulder, P.; Korth, H.-G.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **2000**, *122*, 2355−2360.

(24) Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H. *NIST Chemical Kinetics Database*, version 2Q98; NIST Standard Reference Data, National Institute of Standards and Technology: Gaithersburg, MD, 1998.

TABLE 6. Relative Experimental and DFT-Predicted Rate Constants for Dechlorination at 630 K[a]

compd	$k_{exp,rel}$	$k_{DFT,rel}$
4/4a-2	1.00	1.00
5[b]	$\leq 2 \times 10^{-3}$	4×10^{-3}
6/6b	0.17	1.45
7	4.06	3.16
8/8a-2	0.45	0.62
8/8b	0.82	0.73
9/9a-2	0.66	1.27
11/11a-2	0.29	1.95
12[b]	$\leq 3 \times 10^{-3}$	6×10^{-3}
13/13b	0.25	1.77
14[b]	$\leq 3 \times 10^{-3}$	4×10^{-3}
22[c]	0.04	1.68
23[c]	0.02	0.12
34/34b[d]	1.00	1.00 (86.5)
36/36b[d]	3.39	1.55 (92.0)

[a] The $k_{DFT,rel}$ is derived from $k_{DFT} = K_t \, k_{RRD}$ (see eq 1), using the thermodynamic data from Table 3. The $k_{exp,rel}$ values are taken from Table 1. [b] With the HA for phenol or aniline at C-4 from Table 5. [c] Average experimental data for experiments with **22** + **23** or **23** dissolved in **1** at 621 ± 2 K.[7b] The k_{exp} is obtained by multiplying the global rate constant for disappearance, derived as outlined before (see Table 1, footnote b), with the selectivity to naphthalene as an indicator for RRD: 20% (**22**) and 35% (**23**) yielding 1.93 × 10^{-6} (**22**) and 1.03 × 10^{-6} (**23**) M^{-1} s^{-1}. The HA values for **22** and **23** used are those presented in Table 5 for naphthalene. [d] At 523 K, using conversions for **34** of 19% and for **36** of 51% (see Table 2), k_{exp} values are 1.51 × 10^{-5} (**34**) and 5.11 × 10^{-5} (**36**) M^{-1} s^{-1}. The computed relative rate constants at 630 K are given in parentheses.

endothermal, the preexponential factor for RRD decreases as well. Provided that the subsequent chlorine atom elimination is sufficiently fast, the overall rate constant for hydrodesubstitution of the tautomeric entities is given by $K_t k_{RRD}$, with K_t the equilibrium constant for tautomerization. The computed relative desubstitution rate constants by RRD are compiled in Table 6 using the thermodynamic data from Table 3, supplemented by $k_{exp,rel}$ from Table 1.[25] Despite some minor variations, DFT at this level of theory appears to predict the observed relative rates with an agreeable accuracy. The most predominant factor determining the selectivity is the energy for tautomerization. The large difference in reactivity between **22** and **36** is adequately quantified showing that the latter reacts about 50 times faster with the donor solvent.

It should be emphasized that according to the above calculation it is implicitly assumed that the tautomers are at their equilibrium concentration. The C–C cleavage of 4-hydroxydiphenylmethane (see Introduction) is accelerated by the addition of phenolic compounds, suggesting that tautomerization is a bimolecular process.[8] Similar features have been noted when reacting 1-methoxynaphthalene at 638 K in **1**: 11% of the reagent is converted and the product yields are 2-methyl- and 4-methylnaphthol (30%) and 1-naphthol (60%).[7] On thermodynamic grounds, the rate for hydrodesubstitution of methylnaphthols is expected to be similar to that for 4-chloronaphthol (**34**), which is supposed to be quantitative at this particular (high) temperature (see Table 6). Apparently, in these experiments the total phenolic

concentration was still too low, and tautomerization is (partially) rate limiting. This does not apply to the present results, since the total phenol concentration remains constant and at a high level. The experiments with the phenyl derivatives have been performed in the presence of water to pressurize the reaction vessel. Water may have catalyzed the tautomerization, thereby changing the overall kinetic behavior for dechlorination. However, the experiments with naphthyl derivatives have been conducted in the absence of water, and as can be noted from Table 6, the relative reactivity is still well predicted with eq 1. In that case, small amounts of acid (HCl) formed at the early stage of reaction may already be sufficient to assist the tautomerization. This is further corroborated by the observation that **36** is almost inert under conditions of high dilution while the addition of an organic acid effectively increased the hydrodechlorination. Therefore, we can conclude that the dechlorination of the compounds investigated proceeds via a non-rate-determining tautomeric equilibrium.

Hydrodechlorination: Absolute RRD Rate Constants. According to the preceding section, the experimental (relative) selectivities for hydrodechlorination for the compounds investigated can be predicted quite well by a combination of eq 1 and the appropriate thermodynamic data. However, the absolute experimental rate constants are significantly higher.[26] It should be noted that eq 1 has been developed to quantify the rates for transfer hydrogenation for various aromatic ketones. In both cases, a ketyl radical is formed after the initial hydrogen atom transfer to the heteroatom, but the subsequent steps differ. With the chlorinated enones (and imines), the loss of chlorine will be the product channel. On the other hand, with the aromatic ketones a second bimolecular hydrogen atom abstraction is required to arrive at the hydrogenated compound. Rüchardt concluded that for transfer hydrogenation of the olefinic moiety in styrene derivatives, the activation enthalpy $\Delta H^{\ddagger}$ for initial RRD is less than the required overall reaction enthalpy and that the enthalpy level of the transition state shifts to the reagent side when the RRD becomes less endothermal.[5] This implicitly assumes the presence of an intermediate caged radical pair, emerging directly after the hydrogen transfer, for which the energy content is lower with respect to the transition state. Consequently, a certain degree of reversibility for RRD may be present depending on the depth of the well for the caged radical pair, the enthalpy levels for the transition state, and the product manifold. A pictorial presentation of the various pathways for tautomer **6b** is given in Figure 1.

The entropy change for the conversion of the caged radical pair into two separated species is expected to be

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(25) Applying $\Delta H_{RRD} = HA + 75.2$, with HA the hydrogen affinity (see Table 3) and 75.2 kcal mol^{-1} the benzylic BDE(C–H) for **1**, as computed by DFT (ref 20).

(26) It should be noted that the HAs in Table 3 for the chloro-substituted aromatic alcohols and amines refer to the formation of a chlorine–arene π-complex. Thus, without this DFT anomaly, and equating, for example, the HA for **6b** to that for **3b** the ratio between the experimental and calculated rate constant is about 10^6. Recently, we have encountered a similar feature while investigating the thermal stability of *O*-benzyl ketoximes (R$_1$R$_2$C=NOCH$_2$Ph) in **1**. After hydrogen transfer to nitrogen, a N–O cleavage occurs in R$_1$R$_2$C(•)NHOCH$_2$-Ph yielding the imine, R$_1$R$_2$CNH, and benzyl alcohol (after hydrogen abstraction from the solvent). Computations have revealed that the N–O bond in the adduct radical is weak, suggesting that the cleavage reaction is extremely fast. (b) Sheeller, B.; Pratt, D. A.; Walton, J. C.; Korth, H.-G.; Mulder, P.; Ingold, K. U. Manuscript in preparation.
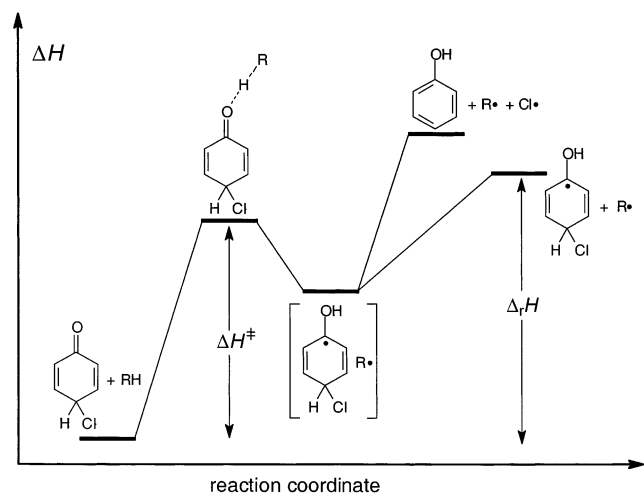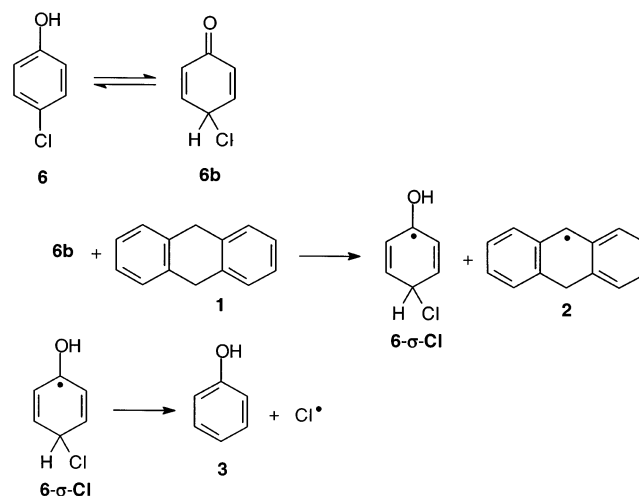
FIGURE 1. The various pathways involved in the reverse radical disproportionation (RRD) mechanism; enthalpy levels are not scaled.

quite modest. Conversely, the entropy gain for direct chlorine elimination is estimated to be around 13.5 cal mol^{-1} K^{-1}.[22] As a result, the latter reaction may be favored due to an enthalpy/entropy compensation effect.[27] According to this thermokinetic analysis, the dynamic behavior of the chlorinated enones and imines may well be the first example of an irreversible RRD, in contrast with the transfer hydrogenation of styrenes or aromatic ketones. From this study it can be concluded that the intrinsic activation enthalpy for any RRD is certainly less than the reaction enthalpy, and it seems reasonable to postulate that an Evans–Polanyi-type relation exists between the two parameters. This may explain why predicting relative rates by using the DFT-computed HA values, though identified as to be constantly underestimated, still is a meaningful approach. For a thorough kinetic analysis additional (temperature dependent) experiments are required to assess the parameters for each individual step displayed in Figure 1.

Thermal Stabilities of Phenols and Anilines. In a non-hydrogen donor solvent, such as biphenyl, **6** and **13** are thermally not stable at 630 K, while **36** exhibited no reactivity at 523 K. The enone/imine tautomers of these compounds may serve as hydrogen donors due to the easily transferable hydrogens (see Table 5) but such a mechanism can be discarded when considering their equilibrium concentrations. Alternatively, the tautomers may be a source for chlorine atoms through a (slow) carbon–chlorine bond cleavage, acting as an initiation reaction.[28] Hydrogen abstraction by the chlorine atoms from **6** or **13** yields the corresponding phenoxyl or the anilinyl radical. Addition of the incipient oxygen or

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(27) The rate constant for Cl elimination, k_{elim}, for the ketyl radical (see Figure 1) can be estimated by using the adduct of chlorine to benzene as a model. For C$_6$H$_6$Cl → C$_6$H$_6$ + Cl, $\Delta_r H = 7.2$ kcal mol^{-1}, and according to $10^{15}\exp(-\Delta_r H/RT)$ implies a k_{elim} of 3×10^{12} s^{-1} at 630 K (ref 22).
(28) The rate constant for C–Cl cleavage, e.g. 4-ClPhOH (**6**) → **6b** → PhO• + Cl, can be estimated by using $10^{15}\exp(-\Delta_r H/RT)$, with $\Delta_r H$ the overall reaction endothermicity. With $\Delta_r H$ of 70 (**6**), 74 (**13**), and 69 (**36**) kcal mol^{-1} (data from ref 14d and Table 5), rate constants (s^{-1}) of 4.9×10^{-10} (**6**) and 1.5×10^{-11} (**13**) at 630 K and 1.6×10^{-14} (**36**) at 523 K were estimated.

SCHEME 12

nitrogen-centered radical to the carbon carrying the chlorine in **6** or **13**, followed by elimination of Cl renders a radical chain mechanism, which ultimately leads to the production of oligomers. Interestingly, **13** is converted almost quantitatively with a concomitant formation of HCl, whereas **6** under the same conditions produces only 11% HCl (with a 78% recovery of the starting material). On thermokinetic grounds, the rate of initiation for **13** is predicted to be somewhat slower.[28] Therefore, this behavior may well be related to a variation in the dynamic properties of the O- and N-based radicals. Anilinyl possesses a higher spin density on nitrogen providing an enlarged intrinsic reactivity, and polymers of the type 4-Cl-(PhNH)$_n$-H may emerge by means of an addition/elimination mechanism.[29] At lower temperatures, the initiation rate decreases, which explains the thermal stability of **36**.[28] The addition of a phenoxyl radical to unsaturated moieties is extremely slow; instead, a radical–radical coupling predominates, serving as a termination reaction.[30] These (pyrolytic) processes will be sufficiently curtailed when a hydrogen donor solvent such as **1** is present, by reducing the phenoxyl or the anilinyl radical concentration.

Amine Coupling Reactions. In all the experiments with (added) arylamines at relatively high concentration and in the presence of an acid, we noted the formation of diarylamines. This condensation-type reaction can be associated with tautomerization as well. For example, 4-chloroaniline (**13**) may react with its imine according to a transamination mechanism, involving the addition of –NH$_2$ to the (protonated) imine as presented in Scheme 13.[31] The in situ formed chlorodiarylamines will be subjected to hydrodechlorination by RRD. According to DFT data, the diarylamines compounds are more susceptible to hydrogen transfer (RRD) than the corresponding arylamines mainly due to a lower energy of tautomerization.[32]

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(29) Such a reaction has been identified in the photoinduced polymerization of 4-chloroaniline: Hashimoto, Y.; Mafuné, F.; Kondow, T. *J. Phys. Chem. B* **1998**, *102*, 4295–4300.
(30) See ref 6, footnote 25.
(31) An anonymous referee suggested that after coupling, NH$_3$ can be eliminated (through a 1,4-elimination through a six-centered transition state) leading to **20** directly.

SCHEME 13
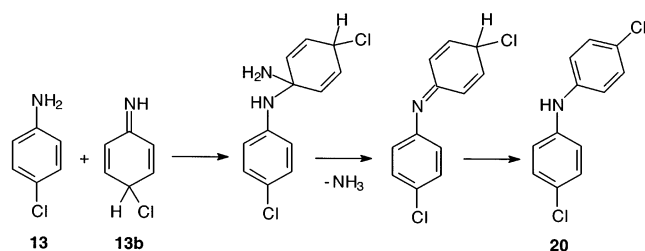
Conclusion

In this work we have demonstrated that hydrodesubstitution of chlorinated aromatic compounds with a hydroxyl or amino group at the C-2 or C-4 position in a hydrogen donor solvent, by means of a reverse radical disproportionation (RRD), is surprisingly facile. The enone/imine tautomers of the chloroaromatics, present at the elevated reaction temperatures, are identified as the reactive intermediates. Analysis of their dynamic behavior suggests that the RRD reaction is irreversible. The selectivities could be adequately predicted by means of DFT computations on the B3LYP/6-31G(d,p) level of theory.

Experimental Section

Materials. All chemicals were commercially available and, when necessary, were purified to $\geq 98\%$ (checked by GC analysis) by recrystallization or sublimation.

Liquid-Phase Experiments. The experimental procedure has been described in detail before.[6] In short, a Pyrex tube of ca. 2 mL was charged for about one-fourth (in volume) with substrate, hydrogen donor solvent, dibenzofuran (or biphenyl)

as an internal standard, and water (for the benzene derivatives only). Prior to sealing of the tube, air was replaced by helium in 3 freeze–pump–thaw cycles. After heating in a thermostat-controlled furnace, the tube was cooled rapidly and decapped. Then, water was rapidly added. Subsequently ca. 0.5 mmol of external standard (2-methoxynaphthalene) in 5 mL of dichloromethane and 5 mL of diluted HNO_3 were added, and the reaction mixture was extracted with dichloromethane (3 × 5 mL). For the arylamines, diluted NaOH was added to the aqueous layer to reach pH 14, followed by extraction with dichloromethane (3 × 5 mL). Subsequently, the aqueous layer was acidified with diluted HNO_3 to neutral pH, and extracted with dichloromethane (3 × 5 mL). A sample of the unified organic layers was dried over molecular sieves. The aqueous layer was divided in portions, the pH was verified, and if necessary, the solution was acidified by diluted HNO_3.

Analysis. The analyses were performed on an HP 5890A gas chromatograph equipped with a CP-Sil-5-CB capillary column, 50 m × 0.32 mm i.d., 0.4 μm film thickness, using hydrogen as the carrier gas. Unknown products were identified on a GC-MS (HP 5890A-HP 5972) with a similar column and helium as the carrier gas. Quantitative analyses were performed with GC-response factors obtained from calibration with authentic samples or by standard estimation methods. The HCl concentration was determined potentiometrically with a standard solution of $AgNO_3$ on an automatic titrator (Mettler DL-25).

Method of Calculation. The calculations were performed with Gaussian 98 rev. A.7, using the B3LYP method with the 6-31G(d,p) basis set for geometry optimizations and vibrational frequency calculations, using the unrestricted formalism for the radicals.[33] Zero-point vibrational energies were scaled by a factor of 0.9805; the energy data presented in this paper refer to 298 K.

Supporting Information Available: Cartesian coordinates and electronic energies of the DFT computations for molecules and radicals as presented in Table 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) With the HAs for the unsubstituted species, see Table 3, the relative (to 4-chloro-1-naphthylamine, **36**) rate constant, $k_{DFT, rel}$, is 14 on a per site basis for di(4-chloronaphthyl)amine. Thus, in situ formed di(4-chloronaphthyl)amine will be dechlorinated much faster and explains our observation that in the experiments with **36** only dinaphthylamine, **37**, was found. The $k_{DFT, rel}$ (to 2-chloro-aniline, **11**) is 1.8 for di(2-chlorophenyl)amine, and $k_{DFT, rel}$ (to 4-chloro-aniline, **13**) is 3.5 for di(4-chlorophenyl)amine. These relative rates suggest that in experiments with **11** or **13** chlorophenylamines may be observed as reaction products, which is indeed the case, see Table 1 (footnote f).

(33) *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.