J. Org. Chem. **2001,** *66,* 6611−6619

Thermal Reduction of 7*H*-Benz[*d,e*]anthracen-7-one and Related Ketones under Hydrogen-Transfer Conditions

Peter Mulder,*,† Sven Hemmink,† Martine I. De Heer,† Marco Lupo,† Danilo Santoro,† and Hans-Gert Korth*,‡

Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands, and the Institut für Organische Chemie, Universität Essen, D-45117 Essen, Germany

p.mulder@chem.leidenuniv.nl

Received March 20, 2001

In the presence of hydrogen donor solvents and at elevated temperatures, aromatic ketones can be selectively deoxygenated to the corresponding hydroaromatic compounds. The kinetics for reduction of 7*H*-benz[*d,e*]anthracen-7-one (benzanthrone, **6**) into 7*H*-benz[*d,e*]anthracene (benzanthrene, **1**) in 9,10-dihydroanthracene (**3**) solvent has been investigated in detail. The relatively slow hydrogenation of **6** is due to reversibility of the initial hydrogen-transfer step according to a reverse radical disproportionation (RRD). The dynamics could well be rationalized using the energetics of species computed by density functional theory (DFT). The application of hydrogen donors such as **1** as a hydrogen-transfer agent, although favorable in terms of a low benzylic carbon−hydrogen bond dissociation enthalpy, is limited due to the slow self-hydrogenation, which in case of **1** gives 5,6-dihydro-4*H*-benz[*d,e*]anthracene (**7**).

Introduction

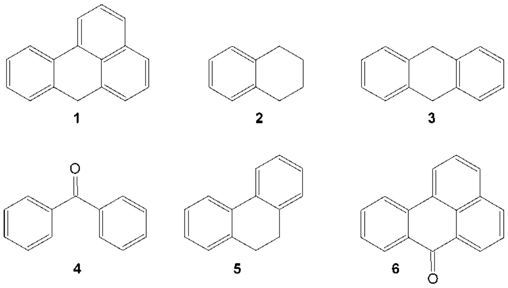
At elevated temperatures, hydroaromatic solvents with weakly bonded (benzylic-type) hydrogen atoms can act as thermal reducing agents.[1] For example, it has been demonstrated that styrenes,[1a] fullerenes,[1a] quinones,[1a] aromatic nitro and nitroso compounds,[1a] substituted naphthalenes,[1b,c] and native lignins[1d] can be reduced in this way. In the first step, a hydrogen atom is shuttled from the donor solvent (RH) to an unsaturated moiety (eq 1). This chemical transformation is known as the reverse radical disproportionation, RRD, and plays an important role in the liquefaction of coal. Subsequently, a second hydrogen atom is transferred, according to eq 2, yielding the hydrogenated product.

$$R^1R^2C{=}CH_2 + RH \rightarrow R^1R^2C(^\bullet)CH_3 + R^\bullet \qquad (1)$$

$$R^1R^2C(^\bullet)CH_3 + RH \rightarrow R^1R^2CHCH_3 + R^\bullet \qquad (2)$$

In principle, the activation enthalpy for eq 1 is governed by the reaction enthalpy, because the reverse reaction, a radical−radical disproportionation, is a near diffusion-controlled process. The temperature at which the thermal hydrogenation occurs at an appreciable rate depends strongly on the thermodynamic properties of both the hydrogen donor and hydrogen acceptor molecules. The relative RRD capability of donor molecules can be directly derived from the respective benzylic carbon−hydrogen bond dissociation enthalpy, BDE(C−H). For example, one of the most reactive hydrogen donors, 7*H*-benz[*d,e*]anthracene (benzanthrene, **1** (Scheme 1)) contains a benzylic BDE(C−H)[2a,b] of as low as 64 kcal mol^{-1}, compared to 83 kcal mol^{-1} for a less efficient donor solvent such as 1,2,3,4-tetrahydronaphthalene (tetralin, **2**).[2c] This implies that, provided eq 1 is the rate-determining step (i.e., $v_2 \gg v_{-1}$), the reduction rate at 300 °C by **1** will be more than 10^7 times faster than **2**. Furthermore, in the reduction of, e.g., α-methylstyrene with a mixture of **1** and 9,10-dihydroanthracene (**3**), **1** may serve as a hydrogen-transfer agent (catalyst)[3] since it is not consumed but recycled by the auxiliary donor solvent.[4]

Scheme 1



However, the efficiency of **1** appears to be less than anticipated on the basis of enthalpic considerations. In our study on the cleavage of α-phenoxyacetophenone at around 300 °C, eqs 3−4, we observed that the addition

---

† Leiden University.

‡Universität Essen.

[1] (a) Rüchardt, C.; Gerst, M.; Ebenhoch, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1406−1430 and references therein. (b) Arends, I. W. C. E.; Mulder, P. *Energy Fuels* **1996**, *10*, 235−242. (c) Dorrestijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder, P. *J. Anal. Appl. Pyrol.* **2000**, *54*, 153−192. (d) Dorrestijn, E.; Kranenburg, M.; Poinsot, D.; Mulder, P. *Holzforschung* **1999**, *53*, 611−616.

[2] (a) Bausch, M. J.; Gostowski, R.; Jirka, G.; Selmarten, D.; Winter, G. *J. Org. Chem.* **1990**, *55*, 5805−5806. (b) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510−517. (c) Laarhoven, L. J. J.; Mulder, P. *J. Phys. Chem. B* **1997**, *101*, 73−77. (d) Malhotra, R.; McMillen, D. F. *Energy Fuels* **1990**, *4*, 184−193.

[3] Morgenthaler, J.; Rüchardt, C. *Eur. J. Org. Chem.* **1999**, *2219*, 9−2230.

[4] The 9,10-dihydroanthracenyl radicals decay through disproportionation. For benzanthrenyl radical, without a reactive hydrogen atom at the β-position, disproportionation with 9,10-dihydroanthracenyl recycles **1**.

10.1021/jo015637v CCC: $20.00 © 2001 American Chemical Society
Published on Web 09/08/2001

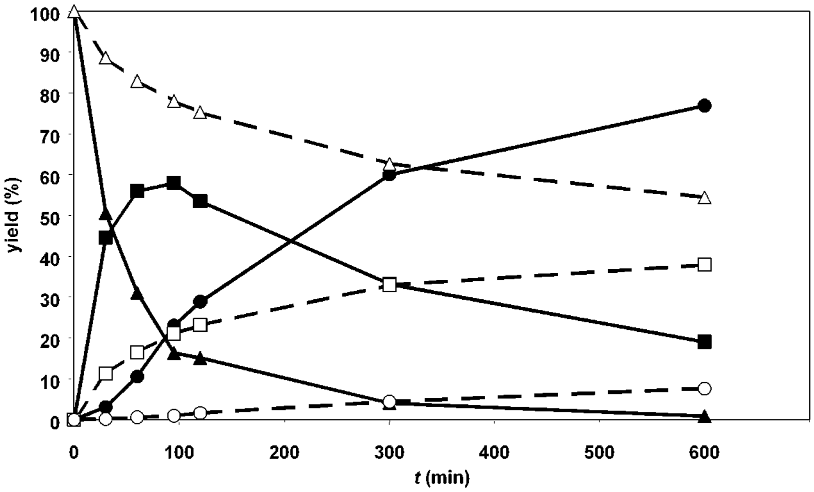


Figure 1. Conversion of benzanthrone (**6**) and 9,10-dihydroanthracene (**3**) at 300 °C with $[\mathbf{6}]_0 = 0.42$ M and $[\mathbf{3}]_0 = 4.27$ M. Solid lines: **6** (▲), benzanthrene (**1,** ■), and 5,6-dihydro-4*H*-benz[*d*,*e*]anthracene (**7**, ●). Dashed lines: **3** (△), anthracene (**11,** □), and 1,2,3,4-tetrahydroanthracene (**12**, ○).

of **1** to **3** (with a BDE(C−H)[2d] of 77 kcal mol^{-1}) afforded only a modest accelerating effect on the rate of disappearance of the substrate.[5]

$$\mathrm{PhC(O)CH_2OPh + RH \rightarrow PhC(^{\bullet})OHCH_2OPh + R^{\bullet}} \quad (3)$$

$$\mathrm{PhC(^{\bullet})OHCH_2OPh \rightarrow PhC(O)CH_3 + PhO^{\bullet}} \quad (4)$$

The mechanistic and dynamic aspects of RRD for the hydrogenation of olefinic moieties have been well documented for a range of donor and acceptor molecules.[1a] For the transfer hydrogenation of carbonyl groups, however, these features are less well understood. For example, in the thermal reduction of benzophenone (**4**), the expected product (benzhydrol) is formed only in minute amounts. Instead, the dehydroxylated compound (diphenylmethane) emerges as the most prominent product.[6] The formation of the alcohol can be easily rationalized analogously to eqs 1−2 and involves the formation of an intermediate ketyl radical. However, the precise mechanism for the loss of the hydroxyl in a nonpolar environment remains somewhat obscure. A mechanism has been postulated in which the intermediate alcohol dimerizes to an ether with loss of water. Next, hydrogen atom abstraction from the ether provides the diphenylmethane and benzophenone.[6] Recently, we have demonstrated that the quantitative conversion of *o*-hydroxyl benzylic alcohol, dissolved in **1**, **3**, or 9,10-dihydrophenanthrene (**5**), into *o*-hydroxytoluene proceeds through an ionic intermediate. An acid-catalyzed removal of the hydroxyl group affords the corresponding benzylic carbocation, which abstracts a hydride from the hydroaromatic solvent.[7]

On the basis of the foregoing, a strong reducing reagent such as benzanthrene (**1**) could well be obtained in situ from the readily available 7*H*-benz[*d*,*e*]anthracen-7-one (benzanthrone, **6**). In this study, the reactivity of benzanthrone and related aromatic ketones in the presence of donor solvents has been investigated to obtain insight into the dynamics of their reduction pathways. To assess the thermokinetic behavior of the (intermediate) species, the benzylic BDE(C−H)s need to be known with some precision. Since pertinent and consistent experimental information is scarcely available, we have computed the BDEs for a large set of compounds and related radicals by density functional theory (DFT) employing the B3LYP/6-31G(d,p) method.

Results

Benzanthrone (6) in 9,10-Dihydroanthracene (3): Products. The product distribution for the temporal conversion of **6** at 300 °C, with **3** as the hydrogen-donor solvent (molar ratio of **6**/**3** = 1:10) is displayed in Figure 1.

The product distributions under various reaction conditions are summarized in Tables S1 and S2 of the Supporting Information. The reduction product is benzanthrene (**1**) with *m*/*z* 216 (M$^+$), which at prolonged reaction time decays into a hydrogenated product with *m*/*z* 218 (M$^+$), according to GC−MS analysis. To isolate this compound for the structural identification, a thermal reaction on a preparative scale was carried out with **6** in tetralin (a solvent that can be easily removed by distillation) at 365 °C. The isolated and purified product was analyzed by NMR spectrometry (including a simulation analysis) and identified as 4,5-dihydro-6*H*-benz[*d*,*e*]anthracene (**7**), and not its isomer 2,3-dihydro-1*H*-benz[*d*,*e*]anthracene (**8**) (Scheme 2). In the Supporting Information, the NMR details are provided.

Some minor products (each with yields of less than 0.5%) were observed as well: a compound with a *m*/*z* 232 (M$^+$) assigned as 7*H*-benz[*d*,*e*]anthracen-7-ol (benzanthrenol, **9**), an isomer of **1**, and at longer reaction times a hydrogenation product of **7** with *m*/*z* 234 (M$^+$). Throughout the experiments with **6** (*m*/*z* 230, M$^+$), a product with *m*/*z* 234 (M$^+$) (100) and *m*/*z* 215 (M$^+$−19) (20) was obtained. The molecular mass of this compound, which could be removed from the reaction mixture by aqueous alkaline extraction, suggests the addition of four hydrogens to **6** with retention of oxygen. By comparing retention times of analogue compounds, this product is ten-

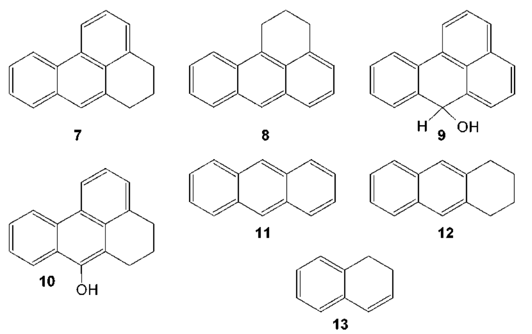
---

[5] Dorrestijn, E.; Hemmink, S.; Hulstman, G.; Monnier, L.; Scheppingen, van W.; Mulder, P. *Eur. J. Org. Chem.* **1999**, *607*, 7−616 (correction *Eur. J. Org. Chem.* **1999**, *1267*, 7).

[6] Choi, C.; Stock, L. M. *J. Org. Chem.* **1984**, *49*, 2871−2875.

[7] Dorrestijn, E.; Kranenburg, M.; Ciriano, M. V.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 3012−3018.

Scheme 2



tatively assigned as a phenolic compound, 5,6-dihydro-7-hydroxy-4*H*-benz[*d,e*]anthracene (**10**). The product ratio (**1** + **7**)/**10** remained rather constant (ca. 30). In preliminary experiments with nonpurified **6**, the yield of **10** could reach a level of 20%. The same result was obtained when the reduction of **6** was carried out in the presence of a large amount of pyridine (see Table S2, experiment no. 2.12).

Next to the reduction of **6**, the self-hydrogenation of **3** yielded anthracene (**11**) and 1,2,3,4-tetrahydroanthracene (**12**) in equimolar amounts. The mass balances for **6** (sum of remaining **6** and the products **1**, **7**, and **10**) and for **3** (sum of the remaining **3** and the products **11** and **12**) were always better than 93%. The overall hydrogen balance could be well described by $2[\mathbf{1}] + 3[\mathbf{7}] + 2[\mathbf{10}] = [\mathbf{11}] - [\mathbf{12}]$.

Benzanthrene is an unstable compound at room temperature in the presence of air, where it is slowly reoxidized to benzanthrone.

Benzanthrone (6) in 9,10-Dihydroanthracene (3): Kinetics. The concentration of **6** was varied in such a way that the ratio **6**/**3** ranged from 1:5 to 1:80. The conversion of **6** remained constant at around 70%; only the rate of hydrogenation of **1** into **7** was slowed when applying a lower initial concentration of **6**. When the concentration of **3** was lowered by dilution with diphenyl ether, the rate of conversion of **6** decreased and became zero in the absence of a hydrogen donor. At first glance, it seems somewhat surprising that the rate of reduction of **6** depends on **3** and not on the in situ generated benzanthrene (**1**), which is a superior hydrogen donor. For example, after 60 min 0.24 M of **1** is obtained when starting with mixture of 4.27 M **3** and 0.42 M **6**.[8a] Addition of an excess of anthracene (a reaction product) retarded the hydrogenation of **6**. The results are collected in Table S2.

Without detailing the mechanism, the experimental rate constant for the disappearance of **6** ($k_{\mathrm{exp},\mathbf{6}}$) was retrieved assuming $v_{\mathbf{6}} = k_{\mathrm{exp},\mathbf{6}}[\mathbf{6}][\mathbf{3}]$ as the kinetic expression. With the data from Table S1 and S2 (experiments 1.1−1.3 and 2.1−2.10), a plot was constructed of $\ln([\mathbf{6}]/[\mathbf{6}]_0)([\mathbf{3}]_0/[\mathbf{3}])$ versus $([\mathbf{6}]_0 - [\mathbf{3}]_0)t$. A quite satisfying linear regression line ($r^2 = 0.96$) was obtained with a slope of $k_{\mathrm{exp},\mathbf{6}} = 7.1 \times 10^{-5}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.[8b]

Isotope Effect on the Hydrogenation of Benzanthrone (6). Experiments were conducted with benzanthrone and mixtures of anthracene or perdeuterated anthracene and 9,10-dihydroanthracene (molar ratio of 1:1) to explore the kinetic isotope effect on the RRD.[9] After 60 min and at 300 °C, the conversion of **6** reached the same level of 24% for both experiments, indicating the absence of a (primary) isotope effect. The molar ratio between 9,10-dihydroanthracene and anthracene dropped from 1:1 to 0.7:1 during reaction.

Integrated MS spectra were disentangled to quantify the H/D distributions in reactants and products. The assumption was made that the degree of the most predominant fragmentation (loosing hydrogen or deuterium) remains constant for alike compounds.

Six isotopomers could be identified for 9,10-dihydroanthracene, denoted as $(H/D)_8An(H/D)_4$ with (H/D_4) as the hydrogens or deuteriums attached to the positions C-9 and C-10. The product ratios were as follows: $H_8AnH_4/H_8AnH_3D/H_8AnH_2D_2 = 0.53{:}0.33{:}0.14$ and $D_8AnH_4/D_8AnH_3D/D_8AnH_2D_2 = 0.05{:}0.41{:}0.54$. The overall molar ratio between $H_8An(H/D)_4$ and $D_8An(H/D)_4$ compounds was 0.93.

In addition, six isotopomers were detected for anthracene with ratios for $H_8AnH_2/H_8AnHD/H_8AnD_2$ of 0.85:0.13:0.02 and for $D_8AnH_2/D_8AnHD/D_8AnD_2$ of 0.21:0.27:0.52, together with a molar ratio between $H_8An(H/D)_2$ and $D_8An(H/D)_2$ compounds of 1.03.

After reaction, the aromatic nuclei containing either H or D are equally distributed in both 9,10-dihydroanthracene and anthracene. Besides, the overall H/D ratio for the (benzylic) C-9 and C-10 positions is around three, identical with that of the starting mixture. The finding underscores that under these reaction conditions the equilibrium $H_8AnH_4 + D_8AnD_2 \rightleftharpoons H_8AnH_2 + D_8AnD_2H_2$ is firmly established. In the absence of benzanthrone, the degree of H/D exchange is still kinetically determined.[10]

The deuterium incorporation in benzanthrene at the benzylic C-7 position, $Bz(H/D)_2$, was higher compared to that in 9,10-dihydroanthracene. A considerable H/D exchange has occurred in the aromatic nucleus as well. Four isotopomers were present with a ratio for $BzHD/BzD_2/DBzD_2/D_2BzD_2$ of 29:62:8:1; nondeuterated benzanthrene (BzH_2) could not be detected.

Finally, in the remaining benzanthrone some 18% H/D exchange had taken place.

Benzanthrone (6) in Other Hydrogen Donors. For comparison, the hydrogenation of benzanthrone was carried out in three other hydrogen-donor solvents: tetralin (**2**), 9,10-dihydrophenanthrene (**5**), and 1,2-

---

[8] (a) Molar densities of the reagents used in this study are not known at the temperatures applied. By volumetric analysis, we could estimate a value of 4.9 M for **3** used in this study at around 300 °C. For other compounds we have assumed the same molar densities and no mixing volumes. With an initial mixture of 0.1967 mmol **6**, 2.0161 mmol **3**, and 0.10 mmol **11**, their concentrations at the reaction temperature are computed as 0.42 M **6**, 4.27 M **3**, and 0.21 M **11**. After a reaction time of 60 min, the absolute amounts were determined as (in mmol): 0.062 (**6**), 0.1118 (**1**), 1.6283 (**3**), and 0.4250 (**11**), or with a constant reaction volume (in M) 0.13 (**6**), 0.24 (**1**), 3.4 (**6**), and 0.9 M (**11**) at 300 °C (see Table S1, experiment 1.2). The latter values are regarded as a typical composition and are used in the further thermokinetic calculations. (b) In this analysis we did not use experiments at extended reaction times (experiments 1.4−1.6, Table S1), since the contribution of the consumption of **3** by self-hydrogenation becomes significant.

[9] Since perdeuterated anthracene is readily available, thermal H/D exchange reaction between **3** and **11** is applied to generate in situ deuterated 9,10-dihydroanthracene. A disadvantage, however, is that the concentration of the deuterated hydrogen donor will increase with reaction time. Hence, the kinetic isotope effect found can only serve as a qualitative indication.

[10] A separate experiment with only a mixture of **3** and D_8AnD_2 (molar ratio of 1:1) showed a reduced degree of H/D scrambling. The results are as follows: $H_8AnH_4/H_8AnH_3D/H_8AnH_2D_2 = 0.80{:}0.16{:}0.04$ and $D_8AnH_4/D_8AnH_3D/D_8AnH_2D_2 = 0.06{:}0.37{:}0.57$, with $H_8An(H/D)_4/D_8An(H/D)_4 = 2.3$; $H_8AnH_2/H_8AnHD/H_8AnD_2 = 0.92{:}0.04{:}0.04$, and $D_8AnH_2/D_8AnHD/D_8AnD_2 = 0.09{:}0.04{:}0.87$, with $H_8An(H/D)_2/D_8An(H/D)_2 = 0.46$.

Table 1. Reduction of Benzanthrone (6) in Various Hydrogen Donor Solvents at 300 °C[a]

			yield (%)					
expt no.	*t* (min)	solvent	**6**	**1**	**7**	**10**	S[c]	v_{rel}[b]
4.1	60	tetralin (**2**)	98.4	1.6	0.0	0.0	99	0.01
4.2	60	9,10-dihydroanthracene (**3**)	31.1	56.0	10.6	2.4	83	1
4.3	60	9,10-dihydrophenanthrene (**5**)	91.0	8.6	0.2	0.2	97	0.08
4.4	60	1,2-dihydronaphthalene (**13**)	85.2	14.0	0.7	0.0	30	0.14
4.5	300	tetralin	86.7	11.7	1.6	0.0	98	0.02
4.6	300	9,10-dihydroanthracene	4.2	33.2	60.0	2.6	63	0.55
4.7	300	9,10-dihydrophenanthrene	27.0	47.6	22.1	3.3	85	0.22
4.8	300	1,2-dihydronaphthalene	72.9	17.6	9.4	0.0	0	0.05

[a] Yields normalized to 100%; products benzanthrene (**1**), 5,6-dihydro-4*H*-benz[*d*,*e*]anthracene (**7**), 7-hydroxy-5,6-dihydro-4*H*-benz[*d*,*e*]anthracene (**10**). Initial molar ratios (**6**/hydrogen donor **2**, **3**, **5**, or **13**) = 15.2, 10.2, 12.2, 15.4. [b] Relative rates for the disappearance of **6** according to first-order kinetics, with experiment 4.2 as the reference. [c] Yield of the donor solvent (S) due to (de)hydrogenation, in experiments 4.8, 1,2-dihydronaphthalene was completely converted into a 1:1 mixture of naphthalene and tetralin.

Table 2. Reduction of Various Aromatic Ketones in 9,10-Dihydroanthracene (3) at 300 °C[a]

	yields (%)				rel rates	
expt no	ketone		product		v_{rel}[e]	v_{rel}[g]
5.1	benzophenone (**4**)	90	diphenylmethane	10	0.10	0.0054
5.2	benzanthrone (**6**)	36	benzanthrene (**1**)	52[b]	1	1
5.3	anthrone (**14**)	62	9,10-dihydroanthracene (**3**)	*c*	0.38	0.0066
5.4	fluorenone (**15**)	83	fluorene	17	0.14	1.27
5.5	xanthone (**16**)	100			0	0.0007
5.6	anthraquinone (**17**)	10	anthrone	79[d]	1.13[f]	4.6

[a] Reaction time 60 min, data from competition experiments with equimolar amounts (ca. 0.2 M) of ketone in **3** and always in the presence of **6**. The degree of conversion of **6** was not affected by the presence of other ketones. [b] For other products see Table S1. [c] The reduction product may be 9,10-dihydroanthracene (**3**) or anthracene (**11**) and cannot be quantified in **3**. [d] Anthrone is partially reduced, see experiment no. 5.3. [e] Relative rates (to **6**) for the disappearance according to first-order kinetics. [f] Per carbonyl group. [g] Predicted relative rates using the $\Delta_{\text{RRD}}H$'s according to Table 3 and the rate constant for RRD according to ref 23.

dihydronaphthalene (**13**). As with **3**, only **1** and **7** were obtained as the major reaction products. Details are given in Table 1.

The documented self-hydrogenation of donor solvent **13** into equimolar amounts of naphthalene and tetralin is faster than the hydrogenation of **6**.[11] Interestingly, although the RRD capacity of **2** and **5** are expected to be the same, conversion of **6** differs markedly in these solvents, i.e., after 300 min 13 vs 73%. This discrepancy may be related to the presence of impurities with different hydrogen-donating properties. For all practical purposes, the synthesis of **1** should preferably be performed in tetralin at more elevated temperatures. In this solvent, the conversion of **6** increases from 13% at 300 °C and 300 min to 99% at 365 °C and 180 min with selectivities to **1** and **7** of 90 and 10%, respectively.

Benzanthrene (1) in 9,10-Dihydroanthracene (3). Since **1** is converted into **7** during the hydrogenation of **6**, this reaction has been studied separately by dissolving **1** in **3** at 300 °C. The temporal product distribution is presented in Table S3. Analysis of the rate data reveals that the decay of **1** is perfectly described by a second-order kinetic expression: $-\,\mathrm{d}([\mathbf{1}])/\mathrm{d}t = k_{\exp,\mathbf{1}}[\mathbf{1}]^2$. From the plot of $[1/[\mathbf{1}] - 1/[\mathbf{1}]_0]$ versus reaction time (see Figure 2) yields a linear regression line ($r^2 = 0.998$) with a slope of $k_{\exp,\mathbf{1}} = 3.81 \times 10^{-4}$ M^{-1} s^{-1}.

Benzophenone (3), Anthrone (14), Fluorenone (15), Xanthone (16), and Anthraquinone (17) in 9,10-Dihydroanthracene. The behavior of some other aromatic ketones in **3** was scrutinized as well by employing competition experiments and in the presence of always the same amount of benzanthrone. Xanthone appeared to be inert, and with the other ketones only the deoxygenated analogues (hydroaromatics) were obtained (see Table 2).

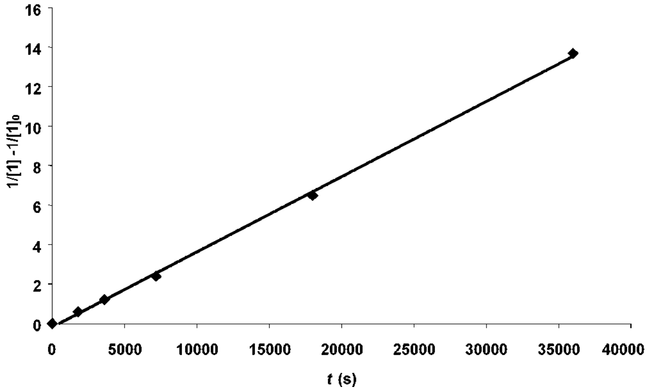
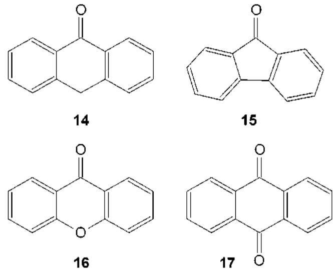


Figure 2. Second-order plot for hydrogenation of 7*H*-benz[*d*,*e*]anthracene (**1**) into 5,6-dihydro-4*H*-benz[*d*,*e*]anthracene (**7**) at 300 °C with $[\mathbf{1}]_0 = 0.42$ M and $[\mathbf{3}]_0 = 4.27$ M.

Scheme 3



The hydrogenation of fluorenone (**15**) has been studied previously (Scheme 3). With **15** in **3**, and at 400 °C, the reduction into fluorene is considerably slower (14%, versus 17% at 300 °C, see Table 2).[6] Another study has revealed that fluorenone in **3** is hydrogenated into

---

(11) Gavalas, G. R.; Allen, D. T. *Int. J. Chem. Kinet.* **1983**, *15*, 219–233.

fluorenol (80%) and fluorene (20%), with a total yield of 50% at 350 °C within 60 min. Upon increasing the polarity of the solvent, the conversion of **15** diminishes, while the product ratio changes in favor of fluorene.[12]

DFT-Computed BDE(C−H)s in Hydroaromatic Compounds and Derived Radical Species. To facilitate the thermokinetic interpretations of our results, the bond dissociation enthalpies, BDE(C−H) and BDE(O−H), for a broad range of compounds and related radicals have been computed by DFT using the B3LYP/6-31G-(d,p)//B3LYP/6-31G(d,p) methodology. In this way, an internally consistent set of values is obtained. The computational results together with available experimental data obtained from literature are presented in Table 3. It should be emphasized that the experimental data are stemming from both gas and liquid-phase studies. Accepting the inherent experimental uncertainties, the results in Table 3 demonstrate that the discrepancy between theory and experiment (with some exceptions) is about 2 kcal mol^{-1}. This underscores the internal reliability of DFT at this level of theory for the computation of BDE's. For the thermochemical assessments throughout the discussion section, the computed values are used unless specified otherwise.

Discussion

Reduction of Benzanthrone into Benzanthrene. The formation of the ketyl radical (**18**) from benzanthrone (**6**) may occur by RRD with 9,10-dihydroanthracene (**3**) or the in situ formed benzanthrene (**1**), eqs 5−6, and simultaneously producing 9,10-dihydroanthracenyl (**19**) or benzanthrenyl (**20**) radicals (Scheme 4). Benzanthrene (**1**) and not benzanthrenol (**9**) is the product of hydrogenation suggesting a fast dehydroxylation under the applied experimental conditions (see below).

For the hydrogen transfer to afford the intermediate **9**, three reaction channels are available: hydrogen abstraction from **3** or **1** (eqs 7−8) or disproportionation with **19**, eq 9. The thermokinetic features of eqs 5−9 need to be established to assess their relative contributions.

The H/D isotope-exchange experiments have shown that the concentration of 9,10-dihydroanthracenyl radical (**19**) can be obtained from the equilibration between **3** and anthracene (**11**):

$$\mathbf{3} + \mathbf{11} \rightleftharpoons \mathbf{19} + \mathbf{19} \qquad (10)$$

The benzanthrenyl radical concentration (**20**) is dictated by a similar equilibrium:

$$\mathbf{1} + \mathbf{11} \rightleftharpoons \mathbf{20} + \mathbf{19} \qquad (11)$$

From the product distributions in Table S1 and S2 (Supporting Information), together with the enthalpic data from Table 3, average concentrations for **19** and **20** at 300 °C can be estimated as 1.2×10^{-6} and 4.7×10^{-4} M, respectively.[14] The kinetic analysis reveals that disproportionation with 9,10-dihydroantracenyl (eq 9) is the most important product-forming step; the hydrogen atom abstractions (eqs 7−8) are relatively slow due to the endothermicity of these reactions. Moreover, the reverse of eq 6 is at least 2 orders of magnitude faster than the product-forming step.[15] This implies that the first step (RRD) in the hydrogenation of benzanthrone with **1** is reversible under these conditions. The rate expression

Table 3. Experimental and B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) Computed Benzylic C−H Bond Dissociation Enthalpies (kcal mol^{-1}) in Hydrogen-Donor Molecules and Radicals and BDE(O−H) in Ketyl Radicals at 298 K

compd	BDE_{exp}	BDE_{DFT}	$BDE_{exp} - BDE_{DFT}$
toluene	89.6 ± 1.0^{a}	88.6	1
ethylbenzene	87.0^{b}	85.7	1.3
cumene	83.2^{c}	84.0	−0.9
cumyl	47.1^{c}	49.1	−2.0
diphenylmethane	82 ± 1^{d}	79.7	2.3
fluorene	80 ± 1^{d}	79.5	0.5
1,2-dihydronaphthalene (1-H) (**13**)		81.0	
1,2-dihydronaphthalene (2-H) (**13**)		76.3	
1,4-dihydronaphthalene		72.9	
1,2,3,4-tetrahydronaphthalene (tetralin) (**2**)	83.0 ± 1.5^{e}	83.6	−0.6
1,2-dihydronaphthalen-2-yl		32.4	
1,2-dihydronaphthalen-1-yl		27.7	
9,10-dihydroanthracene (**3**)	77^{f}	75.2	2.5
1,2-dihydroanthracene (1-H)		81.0	
1,2-dihydroanthracene (2-H)		76.7	
1,4-dihydroanthracene		72.1	
1,2,3,4-tetrahydroanthracene (1-H) (**12**)		82.3	
9,10-dihydroanthracenyl (**19**)	43.2^{f}	42.9	0.3
9,10-dihydrophenanthrene (**5**)		84.2	
9,10-dihydrophenanthrenyl		31.9	
Phenalene (**27**)	62 ± 3^{g}	59.6	2.4
2,3-dihydrophenalene		83.3	
2,3-dihydrophenalen-1-yl		46.3	
7*H*-benz[*d*,*e*]anthracene (**1**)	64 ± 3^{g}	65.4	−1.4
6*H*-benz[*d*,*e*]anthracene (**22**)		60.3	
4*H*-benz[*d*,*e*]anthracene (**23**)		61.3	
3*H*-benz[*d*,*e*]anthracene (**24**)		53.5	
1*H*-benz[*d*,*e*]anthracene (**25**)		55.5	
5,6-dihydro-4*H*-benz[*d*,*e*]-anthracene (4-H) (**7**)		83.7	
5,6-dihydro-4*H*-benz[*d*,*e*]-anthracene (6-H) (**7**)		83.2	
5,6-dihydro-4*H*-benz[*d*,*e*]-anthracen-4-yl (**26**)		45.8	
7*H*-benz[*d*,*e*]anthracen-7-ol (**9**)		59.4	
anthrone (**14**)		71.7	
xanthene	75.5 ± 1.5^{d}	72.3	3.2
benzophenone ketyl	41.6 ± 1.5^{h}	38.5	3.1
anthrone ketyl		36.9	
xanthone ketyl		34.9	
anthraquinone ketyl		45.0	
fluorenone ketyl		42.1	
benzanthrone ketyl (**18**)		44.4	
9,10-dihydro-anthrol-9-yl		43.6^{i}	

[a] Reference 13a. [b] Reference 13b. [c] Reference 13c. [d] Reference 2b. [e] Reference 2c. [f] Reference 2d. [g] Reference 2a. [h] Reference 13d. [i] BDE for the C_{10}−H bond in the radical.

---

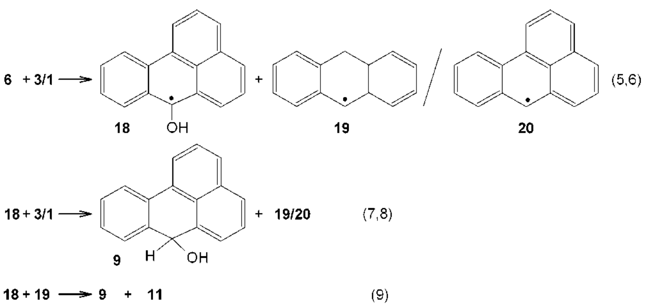
[12] Ebenhoch, J. Ph.D. Dissertation, Universität Freiburg, **1996**.

[13] (a) Tsang, W. In *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenberg, A., Liebman, F., Eds.; Black Academic and Professional: London, 1996; pp 22−58. (b) Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5−10. (c) Laarhoven, L. J. J.; Born, J. G. P.; Arends, I. W. C. E.; Mulder, P. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2307−2312. (d) Arnaut, L. G.; Caldwell, R. A. *J. Photochem. Photobiol, A: Chem.* **1992**, *65*, *1992*, 15−20.

[14] With $\Delta_{10}S = \Delta_{11}S = 0$ and using $\Delta_{10}H = 32.3$, and $\Delta_{11}H = 22.5$ kcal mol^{-1} from Table 3. At 300 °C, K_{10} is 4.8×10^{-13}, and combined [**11**] = 0.9 M,[8a] and [**3**] = 3.4 M,[8a] yields [**19**] $=1.2 \times 10^{-6}$ M; with $K_{11} = 2.6 \times 10^{-9}$, and [**1**] = 0.24 M[8a] provides [**20**] = 4.7×10^{-4} M.

[15] The kinetic parameters suggested by Savage have been used for hydrogen atom abstraction reactions: $A = 10^{8}$ M^{-1} s^{-1}(per hydrogen) $E_a = 16 + 0.35\Delta_rH$ (exothermic), and $E_a = 16 + 0.65\ \Delta_rH$ (endothermic) kcal mol^{-1}, with Δ_rH as the reaction enthalpy.[16] With $k_7 = 3.8 \times 10^{-2}$ ($\Delta_7H = 15.8$ kcal mol^{-1}), $k_8 = 5.1$ ($\Delta_8H = 6.0$ kcal mol^{-1}), and estimating that $k_9 = k_{-6} = 10^{8}$ M^{-1} s^{-1} at 300 °C combined with the concentrations of **3**, **1**, **19**, and **20** in refs 8a and 14, provides the relative rates of $v_7/v_8\ /v_9/v_{-6} = 1.1 \times 10^{-3}$:$1.0 \times 10^{-2}$:1:250.

Scheme 4



for disappearance of benzanthrone (**6**) can now be presented as:

$$-\mathrm{d}[\mathbf{6}]/\mathrm{d}t = [k_9 K_6 K_{10}/K_{11}][\mathbf{3}][\mathbf{6}] \qquad (12)$$

With the enthalpic data from Table 3, eq 12 is reduced to $-\mathrm{d}[\mathbf{6}]/\mathrm{d}t = 1.8 \times 10^{-12} k_9[\mathbf{3}][\mathbf{6}]$.[17] Combination with the experimentally determined $k_{\mathrm{exp},\mathbf{6}}$ of 7.1×10^{-5} M^{-1} s^{-1}, furnishes a rate constant for disproportionation of 9,10-dihydroanthracenyl (**19**) with ketyl **18** of $k_9 = 3.9 \times 10^7$ M^{-1} s^{-1}at 300 °C.

In the absence of significant steric interactions, the rate for disappearance of carbon-centered radicals by radical–radical interaction is at the diffusion-controlled limit. The rate constant (k_{dis}) merely reflects the transport properties of the solvent rather than the nature of the encountering species.[18,20] Typically, k_{dis} is about 2×10^{10} M^{-1} s^{-1} at 300 °C. The two product channels are recombination (k_r) and disproportionation (k_d); the ratio ($k_\mathrm{d}/k_\mathrm{r}$) strongly depends on the type of radicals involved.[21] A linear relationship between $\ln(k_\mathrm{d}/k_\mathrm{r})$ and the reaction enthalpy for disproportionation ($\Delta_\mathrm{d}H$) has been suggested, which can be rewritten as eq 13.[21,22]

$$\ln(k_\mathrm{d}) = 13.6 - 0.16\Delta_\mathrm{d}H \qquad (13)$$

With Δ_9H of -16.5 kcal mol^{-1}, eq 13 yields a k_9 ($= k_\mathrm{d}$) of 1×10^7 M^{-1} s^{-1}, in good agreement with our experimental value of 3.9×10^7 M^{-1} s^{-1}.

The reaction entropy for disproportionation is close to zero, and on the basis of microscopic reversibility, eq 13 can also be used to calculate the preexponential factor for the RRD, $k_{\mathrm{RRD}} = k_\mathrm{d}\exp(-E_{\mathrm{a,RRD}}/RT)$. This implies that the variation in the reactivity of a hydrogen donor cannot be derived exclusively on an activation enthalpy consideration.[23]

Thus, benzanthrene can be applied as a hydrogen transfer agent only when the subsequent step is sufficiently fast. We can estimate that with the inherently elevated concentration of benzanthrenyl (see above), which is a direct consequence of the low BDE(C–H) in **1**, a pseudo-first-order rate constant of 10^5 s^{-1} or higher for the incipient radical species is required to circumvent the reversibility. These findings also explain why the rate for reductive cleavage of α-phenoxyl-acetophone (see Introduction) is accelerated only modestly when adding **1** to **3**. The actual RRD by **1** is faster (eq 3) but the following fragmentation of the ketyl radical into phenoxyl and acetophenone (eq 4) is too slow to compete effectively with the back hydrogen atom transfer to the benzanthrenyl radical. In the past, we have estimated a rate constant for eq 4 as about 10^6 M^{-1} s^{-1}.[24] Now, an upper limit of 10^4 M^{-1} s^{-1} seems to be more in line with the current insights and can be related to the high intrinsic activation barrier for the reverse of eq 4, the addition of a phenoxyl radical to a double bond.[25]

Hydrogenation of Benzanthrene. The hydrogenation of benzanthrene (**1**) follows a second order (in **1**) reaction mechanism**.** At the high temperatures employed, an appreciable radical concentration can be envisaged to establish a dynamic equilibrium between **1** and its radical (**20**). Delocalization of the unpaired electron[26] in **20** creates a number of reactive sites and hydrogen transfer yields an isomeric mixture of 7*H*-benz[*d*,*e*]anthracene (**1**), 6*H*-benz[*d*,*e*]anthracene (**21**), 4*H*-benz[*d*,*e*]anthracene (**22**), 3*H*-benz[*d*,*e*]anthracene (**23**), and 1*H*-benz[*d*,*e*]anthracene (**24**). It seems reasonable to postulate that the concentrations of the isomers are established by an overall thermodynamic equilibrium (eq 14, Scheme 5), which is corroborated by the degree of H/D exchange in benzanthrene when a deuterated solvent is used.

Provided that the entropy changes are negligible, the relative concentrations can be approximated by using the benzylic BDE(C–H)s from Table 3 as **1**/**21**/**22**/**23**/**24** = 3.5×10^4:3.9×10^2:9.4×10^2:1:5.8 at 300 °C. This ratio agrees with the general feature that phenanthrene derivatives are thermodynamically more stable than the isomeric compounds with a (linear) anthracene backbone. Compound **7**, the product of hydrogenation of **1**, emerges through two distinct RRD reactions: hydrogen transfer

---

[16] Savage, P. E. *Energy Fuels* **1995**, *9*, 590–598.

[17] Assuming $\Delta_6S = 0$ and with $\Delta_6H = 21.0$ kcal mol^{-1} from Table 3, renders $K_6 = 9.8 \times 10^{-9}$ at 300 °C (see also ref 14).

[18] The k_{dis} for, e.g., cumyl radicals, measured in *tert*-butylbenzene as the solvent, is determined as $4 \times 10^{11}\exp(-3.4/RT)$, i.e., at 300 °C $k_{\mathrm{dis}} = 2 \times 10^{10}$ M^{-1} s^{-1}.[19a] The temperature dependence for a diffusion-controlled rate constant is associated with the change in the solvent's viscosity (η). The viscosity of pure anthracene is 0.39 cP at 300 °C.[19b]

[19] (a) Korthe, T.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. *J. Chem. Soc. Perkin Trans 2*, **1998**, 1553–1559. (b) *Landolt-Börnstein, 6. Auf. Zweiter Band, 5. Teil, Bandteil a (Transportphänomene I)*; Schäfer, K., Ed; Springer-Verlag: Berlin, Heidelberg, New York, 1969; p 174.

[20] Arends, I. W. C. E.; Mulder, P.; Clark, K. B.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 8182–8189.

[21] Manka, M. J.; Stein, S. E. *J. Phys. Chem.* **1984**, *88*, 5914–5919.

[22] Equation 13 is derived from $\ln(k_\mathrm{d}/k_\mathrm{r}) = -10.1 - 0.16\Delta_\mathrm{d}H$.[21] Since $k_{\mathrm{dis}} \approx k_\mathrm{r} > k_\mathrm{d}$, it can be rewritten as $\ln(k_\mathrm{d}) = -10.1 - 0.162\ \Delta_\mathrm{d}H + \ln(k_{\mathrm{dis}}) = 13.6 - 0.16\Delta_\mathrm{d}H$, with k_{dis} from ref 18.

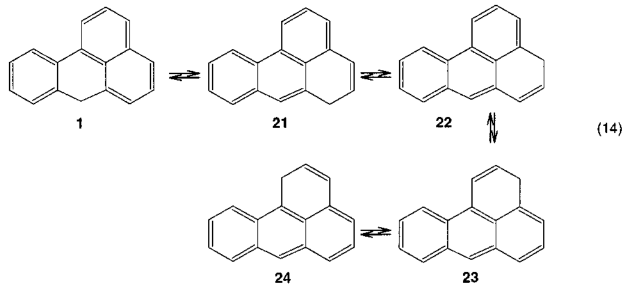
[23] Using eq 13 to derive the A_{RRD} implies that both A_{RRD} and $E_{\mathrm{a,RRD}}$ depend on the reaction enthalpy. This phenomenon is commonly referred to as the isokinetic relationship but may also be imposed by a small enthalpic barrier for disproportionation (Evans–Polanyi principle). Indeed, the factor of 0.16 is quite common for exothermic hydrogen atom abstraction reactions.[20] The rate constant for RRD is presented by $k_{\mathrm{RRD}} = A_{\mathrm{RRD}}\exp(-E_{\mathrm{a,\ RRD}}/RT)$; with $\ln(A_{\mathrm{RRD}}) = \ln(k_\mathrm{d}) = 13.6 + 0.16\Delta_{\mathrm{RRD}}H$ and $E_{\mathrm{a,\ RRD}} = \Delta_{\mathrm{RRD}}H + 3$ with $\Delta_{\mathrm{RRD}}H$ the reaction enthalpy for RRD and a diffusional enthalpy barrier of 3 kcal mol^{-1} for the reverse reaction.[18]

[24] Huang, Y.; Pagé, D.; Wayner, D. D. M.; Mulder, P. *Can. J. Chem.* **1995**, *73*, 2079–2085.

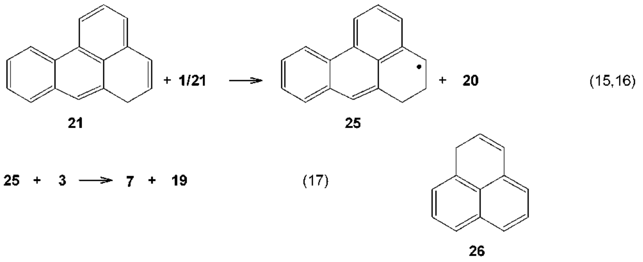
[25] (a) In this particular experiment, the **1**/**3** ratio was 1/16,[5] and according to ref 23 the relative $v_{3,\mathrm{RRD}}$ is expected to be 70. Experimentally, a rate enhancement of only a factor of 5 was found. (b) With a Δ_4H of 12 kcal mol^{-1},[24] $\log(A_4) = 13.4$,[25c] and a rate constant, k_4, of 10^4 s^{-1} leads to $E_{\mathrm{a}4} = 25$ kcal mol^{-1}, thus $E_{\mathrm{a}-4} = 13$ kcal mol^{-1} the reverse reaction: the addition of the phenoxyl radical to the styrene derivative (the enol form of acetophenone). This high activation barrier for phenoxyl may be associated with the extended delocalozation of the free electron into the aromatic ring. In the recombination reaction with methyl, primarily the carbon–carbon coupling occurs,[25d] addition of a phenoxyl to styrene with the spin on carbon yields an adduct with a weak carbon–carbon bond, which will decompose to reactants. (c) Autrey, S. T.; Alnajjar, M. S.; Nelson, D. A.; Franz, J. A. *J. Org. Chem.* **1991**, *56*, 2197–2202. (d) Arends, I. W. C. E.; Louw, R.; Mulder, P. *J. Phys. Chem.* **1993**, *97*, 7914–7925.

[26] According to our DFT calculations, the Mulliken spin densities at positions C-7, C-6, C-4, C-3, and C-1 in the benzanthrenyl radical (**20**) are 0.29, 0.23, 0.23, 0.10, and 0.15, respectively, in good agreement with an EPR study to provide 0.31, 0.22, 0.21, 0.13, and 0.13.[27]

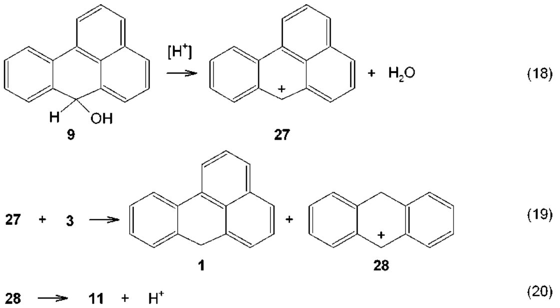
Scheme 5



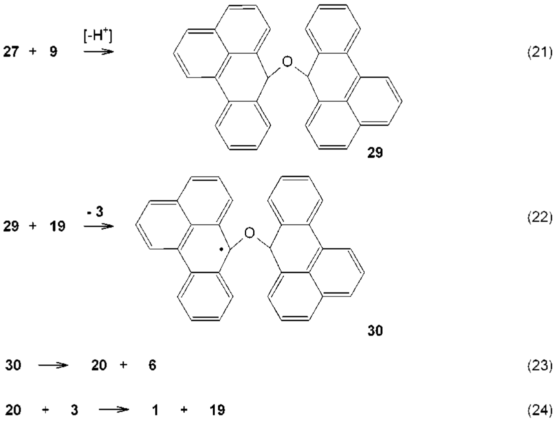
Scheme 6



Scheme 7



Scheme 8



from **1** (eq 15) or **21** (eq 16) to the unsaturated moiety (Scheme 6).[28] Hydrogen abstraction by the intermediate radicals from, e.g., **3**, yields **7** and recycles **1**. With $k_{\mathrm{exp},\mathbf{1}}$ of 3.81×10^{-4} M^{-1} s^{-1}, and the equilibrium concentration for **21**, the RRD rate constants for eq 15 and eq 16 can now be derived as 1.0×10^{-2} and 0.26 M^{-1} s^{-1}, respectively. There is no way to differentiate between these two pathways, since the concentrations of **1** and **21** are equilibrated. Interestingly, as a result of the hydrogenation of **1**, the RRD capacity is greatly diminished. The BDE(C−H) of 83.4 kcal mol^{-1} in **7** creates a donor solvent which is as (un)reactive as tetralin.

The isomers **21** to **24** can be regarded as derivatives of phenalene, **26**. The self-hydrogenation by RRD of **26** follows the same mechanism with a reported rate constant of $9.8 \times 10^4 \exp(-17.9/RT)$ or 1.45×10^{-2} M^{-1} s^{-1} at 300 °C.[1a]

The RRD enthalpy change for eq 16[28] (15.9 kcal mol^{-1}) is somewhat higher compared to that between two phenalene molecules (13.3 kcal mol^{-1}), while the rate constant for reaction 16 derived in this work is about 20 times higher. With phenalene, the agreement between the computed and experimental enthalpy of reaction is quite satisfactory (13.3 vs 14.9 kcal mol^{-1}). The discrepancy is mainly caused by the reported and unexpected low *A* factor, while according to eq 13 a value of 7×10^6 M^{-1} s^{-1} is predicted. A low experimental *A*-factor may arise when the kinetic measurement is obscured by a reversibility of the investigated reaction.

Conversion of Benzanthrenol into Benzanthrene. So far, it has been postulated that the deoxygenation of benzanthrenol (**9**) into benzanthrene (**1**) is a fast process. For this transformation two mechanistic options are feasible: a hydride transfer (Scheme 7) mechanism or the ether mechanism as proposed by Stock (Scheme 8).[6] An alternative route for the decomposition of ether **29** (Scheme 8, eq 22) may be the direct homolysis due to the presence a weak carbon−oxygen bond. However, an assessment of the reaction rates shows that the contribution of this pathway is negligible.[29]

Both routes include the formation of a carbocation. These species may be trapped when an electron-rich aromatic scavenger, e.g. phenol, is added to the reaction medium. In this way, we have demonstrated that a carbocation is the reactive intermediate in the conversion of *o*-hydroxybenzylic alcohol into *o*-hydroxytoluene.[7] However, adding phenol in about a 1:1 ratio to **3** in the hydrogenation of **6** did not yield the expected electrophilic addition products; it merely served as an inert diluent. Stock arrived at this mechanistic rationale for the conversion of benzophenone via benzhydrol to diphenylmethane by studying the reactivity of benzhydrol under various conditions. Ether formation is a bimolecular rate-determining reaction, and occurs at an appreciable rate only when a fairly high concentration of the alcohol is

---

[27] Lewis, I. C.; Singer, L. S. *Magn. Reson. Chem.* **1985**, *23*, 698−704.

[28] In our calculation we have assumed that compounds **21** and **22** are (thermodynamically) identical, and that the ratio **1**/(**21** + **22**) = **1**/**21** = 26, with an average BDE(C−H) for **21** of 61.7 and $\Delta_{16}H$ = 15.9 kcal mol^{-1}.

[29] (a) The ether **29** may also decompose into **20** and an alkoxyl radical which by a fast elimination of a hydrogen atom yields the initial ketone, **6**. According to the our DFT methodology, the BDE(C−H) for the secondary carbon in propane is computed as 97.1 kcal mol^{-1}. By comparing this with the BDE(C−H) in **1** of 65.4 kcal mol^{-1} from Table 3, a resonance stabilization enthalpy (RSE) of 31.7 kcal mol^{-1} is obtained. The BDE(C−O) in diisopropyl ether can be derived as 85.9 kcal mol^{-1}.[29b] Applying the RSE, the BDE(C−O) in **29** becomes 54.2 kcal mol^{-1}. Subsequently, with a preexponential factor for bond homolysis in the liquid phase of $10^{15.2}$ s^{-1},[29c] and with the BDE(C−O) as a measure for the enthalpy of activation, a rate constant for homolysis of **29** is computed as 3.3×10^{-6} s^{-1} at 300 °C. The pseudo first-order rate constant for eq 22 is given by k_{22}[**19**]. According to refs 14 and 15, [**19**] = 1.2×10^{-6} M, and $k_{22} = 2 \times 10^4$ M^{-1} s^{-1} [$\Delta_{22}H$ = −15.8 kcal mol^{-1} from Table 3, and using the BDE(C−H) of **9**] provides k_{22}[**19**] = 2.4×10^{-2} s^{-1}. Hence, the rate of disappearance of **29** will be entirely governed by eq 22. (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, 20899 (http://webbook.nist.gov). (c) Pratt, D. A.; Heer de, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518−5526.

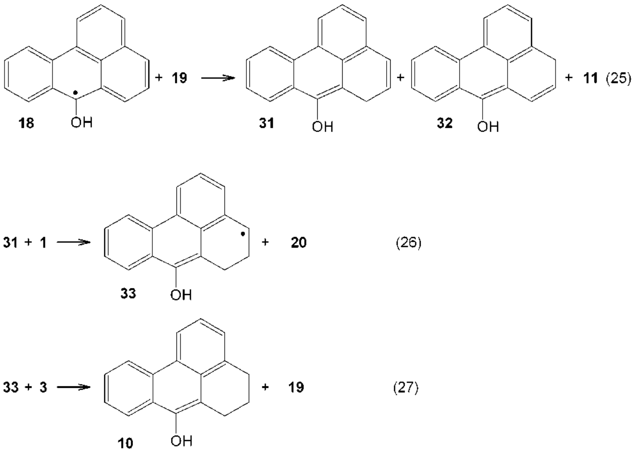
present. We were unable to detect any significant amount of benzanthrenol (**9**), which, combined with the fact that the rate of conversion of **6** is independent of its initial concentration, disfavors the ether mechanism under our reaction conditions.

The nature of the acidic species to create the carbocation remains unclear, the presence of (nonsolvated) protons in a nonpolar environment is counter intuitive. Ketyl radicals in solution are known to be more strongly acidic species than the corresponding alcohols. Further, a substantial difference in pK_a (in water) values has been found for alkyl and aryl ketyls; for example, for *m*-hydroxy benzophenone ketyl and dimethyl ketyl, $Me_2C(^{\bullet})OH$, pK_as of 6.5 and 12, respectively, have been reported.[30] The variation of almost 6 pK_a units can be associated with the better delocalization of the oxygen's lone pair due to the aromatic system. The ketyl derived from benzanthrone is probably an even more acidic species, in accordance with our observation that benzyl alcohol when reacted in the presence of **6** is dehydroxylated for about 50%.[31] The addition of a strong base (pyridine) is expected to reduce substantially the concentration of free ketyl as a result of deprotonation or hydrogen bonding. Consequently the overall reduction rate should be retarded.[32] This, however, appears not to be the case. Clearly, more experimental work is required to unravel the nature of the putative reactive acidic species present in the reduction of aromatic ketones.

That **9** is an intermediate in the hydrogenation of **6** can be concluded from the formation of the phenolic byproduct, **10**. Analogously to the reduction of **1** into **7**, the disproportionation of the ketyl radical (**18**) yields a number of distinct isomeric compounds: **9**, 6*H*-benz[*d,e*]anthracen-7-ol (**31**) and 4*H*-benz[*d,e*]anthracen-7-ol (**32**) (Scheme 9).[33]

The BDE(C−H) in **9** is lower than in **31** or **32**, and a thermal equilibration would render a ratio of **9**/**31**/**32** of 1:2.2:5.3, implying that the phenolic intermediates predominate under these conditions.[34] The final product ratio (**1** + **7**)/**10** remains rather constant at around 30 and is independent of the initial concentrations of **6**, **3** and **1** or the degree of conversion of **1**. By addition of pyridine, this ratio decreases to three, with a concomitant increase in the overall conversion of **6** from 69 to 82%. In that case, the ratio of the intermediate compounds **9**/(**31** + **32**) will be shifted in favor of the thermodynamically more stable hydrogen-bonded phenolic compounds.[35] These results strongly indicate that formation of **31** is reversible under standard reaction conditions. The rate constant for hydrogenation of the olefinic moieties in **31** by benzanthrene (eq 26) is most likely identical to the one determined for the hydrogenation of **21** into **7** (eq 15): i.e., 1×10^{-2} M^{-1} s^{-1}. From our data (see Table 1), it can be inferred that, at longer reaction times, the apparent rate of hydrogenation of **6** is retarded. This is probably the consequence of the build-up of anthracene, which enhances the reformation of the ketyl radical, by a RRD with **9** or **31**. Thus, in the presence of large amounts of anthracene, both reactions 9 and 25 are reversible. Indeed, by addition of anthracene to the reaction mixture, the product ratio increases to 57 and the conversion of **6** drops to 24%. We have used these data to compute the global rate constant for the conversion of **9** into **1** (eq 28).

Scheme 9



$$\mathbf{9} \rightarrow \mathbf{1} \qquad (28)$$

For an fully equilibrated system, the product ratio (**1** + **7**)/**10** is given by $\{(k_{28}K_9)/(k_{26}K_{25})[\mathbf{1}]\}$, and substitition[36] affords a value $k_{28} = 0.43$ s^{-1} at 300 °C, which demonstrates that the reverse reactions will be significant even at low anthracene concentrations.[37] The above analysis underlines the complex dynamics of the reduction by a hydrogen-donor solvent.

---

[30] Bhasikuttan, A. C.; Singh, A. K.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem.* A **1999**, *103*, 4703−4711.

[31] The acidity of such a reaction mixture is underscored by the observation that benzyl alcohol when dissolved in 9,10-dihydroanthracene appeared to be completely inert at 300 °C and 60 min reaction time. However in the presence of **6** (ca. 0.3x the amount of alcohol), 50% dehydroxylation of benzyl alcohol into toluene occurred, while the reactivity of **6** was not affected.

[32] (a) For example, benzophenone ketyl forms a strong hydrogen bond with triethylamine,[32b] a solvent with the same hydrogen bond accepting properties as pyridine.[32c] The reported equilibrium constant at 25 °C for a 1:1 complex between benzophenone ketyl and triethylamine is around 100 M^{-1}. (b) Abe, T.; Kawai, A.; Kajii, Y.; Shibuya. K.; Obi, K. *J. Phys. Chem.* A **1999**, *103*, 1457−1462. (c) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2*, **1989**, 699−711. (d) Recently we have shown the dramatic effect of hydrogen bonding on hydrogen atom abstractions: Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469−477.

[33] According to our DFT calculations, the Mulliken spin densities at positions C-7, C-6, C-4, C-3, and C-1 in the ketyl radical **18** are 0.29, 0.26, 0.25, 0.10, and 0.10, respectively, quite similar to the spin distribution in the benzanthrenyl radical.[26]

[34] It has been assumed that the BDE(C−H)s in **31** and **32** are identical to the ones in **21** and **22**, since the substituent effect (by OH) on benzylic C−H bonds is negligible.[13c] The ratio is computed assuming no difference in entropy between the species, and with the enthalpic data from Table 3. In our calculation we have assumed that compounds **31** and **32** are (thermodynamically) identical, with a (**31** + **32**)/**9** = **31**/**9** = 7.5, and an average BDE(C−H) for **31** of 61.7 kcal mol^{-1} and, hence, $\Delta_{25}H = -18.8$ kcal mol^{-1}.

[35] With the hydrogen bond acidities and basicities from Abraham's list, the equilibrium constant for the hydrogen bonding between pyridine and 1-naphthol (a model for **31** or **32**) is calculated as 58 at 25 °C or 8 M^{-1} at 300 °C.[32c] With 3 M of pyridine in the reaction mixture, the ratio between the hydrogen bonded complex and the free phenol is 24 at 300 °C.

[36] Under conditions of full equilibration for reactions 9 and 25, the product ratio (**1**+**7**)/**10** is given by $[(k_{28}K_9)/(k_{26}K_{25})[\mathbf{1}]]$. With $\Delta_9S = \Delta_{25}S = 0$, $\Delta_9H = -16.5$, $\Delta_{25}H = -18.8$ kcal mol^{-1} (see ref 34) to give $K_9 = 1.96 \times 10^6$, and $K_{25} = 1.48 \times 10^7$. With $k_{26} = k_{15} = 1 \times 10^{-2}$ M^{-1}s^{-1}, combined with [**1**] = 0.10 M (see Table S2, exp. 2.11) and (**1**+**7**)/**10** = 57 (see Table S2, experiment 2.11) yields $k_{28} = 0.43$ s^{-1}.

[37] For example, with [**1**] of 0.24 M,[8a] and $k_{26} = 1.0 \times 10^{-2}$ M^{-1} s^{-1}, the rate of hydrogenation of **31** is about 30 times slower than the RRD with anthracene (**11**) with a k_{-25} of 0.08 M^{-1} s^{-1} and [**11**] = 0.9 M.[8a] For the RRD of **9** with **11**, with $k_{-9} = 0.41$ M^{-1}s^{-1}, a pseudo-first rate constant of 0.37 s^{-1} is calculated, which is comparable with $k_{28} = 0.43$ s^{-1}, the global rate constant for formation of **1** from **9**.[36]

The reaction model as outlined for benzanthone may well be valid for other aromatic ketones. If the relative rates are dictated by the variation in $\Delta_{RRD}H$ only, the predicted relative rates are shown in Table 3. By comparing the experimental and predicted values, it becomes obvious that in this way the differences in reactivity of the various aromatic ketones can be explained only in a semiquantitative fashion.

Conclusion

The selective reduction of aromatic ketones into the hydroaromatic compounds by hydrogen donor solvents has been rationalized by reverse radical disproportionation (RRD) reactions. The dehydroxylation of the intermediate alcohol may occur through a proton transfer from the acidic ketyl radical.

With the aid of DFT-computed enthalpies, providing a consistent set of thermodynamic data, the dynamics of the main reaction pathways for the reduction of benzanthrone have been quantified. Although exhibiting favorably low C−H bond dissociation enthalpies, application of benzanthrene and analogues as hydrogen transfer agents may suffer from reversibility and self-hydrogenation.

Experimental Section

Materials. Compound **1** was synthesized from **6** by reduction with $LiAlH_4$ according to a literature procedure.[38] Purification by sublimation afforded a compound with 94.5% purity (the remaining 5.5% was **6**). Commercially available **6** was sublimed twice. The raw material has a purity of ca. 90%, the nature of the impurity could not be identified, since the GC analysis did not show any other compound. However, upon dissolving **6** in, e.g., toluene, it could be noticed that some black (carbonaceous) insoluble material was present. The color of purified **6** is bright yellow. All other chemicals were commercially available and were purified to ≥99% by distillation or sublimation. The applied 9,10-dihydroanthracene contained 5% of anthracene.

Liquid-Phase Experiments. The procedure has been described in detail previously.[5] In short, a Pyrex tube of ca. 2 mL was charged for about one-fourth (in volume) with substrate, hydrogen-donor solvent, and dibenzofuran as an internal standard. Prior to sealing of the tube, air was replaced by helium in three freeze−pump−thaw cycles. After heating in a thermostat-controlled (GC) furnace, the tube was cooled rapidly and decapped. Then, the reaction mixture was dissolved in toluene and 2-methoxynaphthalene was added as an external standard. The experimental temperature was measured by means of a thermocouple placed through a septum into a Pyrex tube filled with n-eicosane, in proximity of the reaction tubes, and followed by a thermogram. The starting time was taken from the moment a value 5 °C below the final temperature was reached. The overall time to reach the reaction temperature was about 5 min. The temperature stability was ±1 °C. Typically, the reproducibility of the high-temperature liquid-phase experiments was around 2−4%.

Analysis. The analyses were performed on an HP 5890A gas chromatograph (CP-Sil-5-CB capillary column, 50 m, 0.32 mm i.d., 0.4 μm film thickness, and 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 standard estimation methods.

Synthesis of 4,5-Dihydro-6*H*-benz[*d,e*]anthracene (7). A Pyrex tube of 15 mL was charged with 1.4 g (6 mmol) of **6** and 2.6 g (20 mmol) tetralin and subsequently evacuated and sealed as described above. The tube was placed in a thermostat-controlled oven at T = 365 °C for 3 h, cooled to room temperature, and decapped. The reaction mixture was transferred with toluene, and the solvents including naphthalene were removed by vacuum distillation (the apparatus was heated with an IR lamp). The raw product was purified by sublimation, yielding 1.0 g (4.6 mmol, 75%) of **7** (purity 97% as determined by GC). ^1H and ^{13}C NMR spectra (300 MHz) in (solvent $CDCl_3$) were recorded with a Bruker DPX300.

Density Functional Theory Calculations. The calculations were performed using Gaussian 98 rev. A.7 package on an IBM RS6000 computer. The B3LYP method with 6-31G-(d,p) basis set was employed for the geometry optimization and the frequency routines. The ZPVE were scaled by a factor of 0.9805, and the enthalpy of the species were computed at T = 298 K.

Acknowledgment. The authors wish to thank F. Lefebre for recording all NMR spectra and the Hochschulrechenzentrum Essen for the generous allotment of computer resources.

Supporting Information Available: Tables containing data for the temporal conversion and product distribution under various conditions for **6** (Tables S1 and S2) and the temporal conversion of **7** (Table S3). NMR (simulation) data for **7**, Cartesian coordinates and electronic energies of the DFT computations. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015637V

---

[38] Gerst, M.; Morgenthaler, J.; Rüchardt, C. *Chem. Ber.* **1994**, *127*, 691−696.