The Reduction of α-X-Acetophenones (X = PhO, Br, Cl) in Hydrogen-Donating Solvents at Elevated Temperatures

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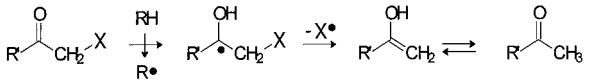
The reduction of α-X-acetophenones (X = PhO, Br, Cl), as model compounds for lignin liquefaction studies, has been investigated in the presence of a hydrogen-donating solvent such as 9,10-dihydroanthracene (AnH_2) or 2-propanol, between 373 and 573 K. With α-phenoxyacetophenone (PAP) in AnH_2, acetophenone and phenol have been obtained with high selectivities. The mechanism involves the reverse radical disproportionation (RRD) with AnH_2. Hydrodebromination of α-bromoacetophenone (BrAP) is quantitative at 423 K using AnH_2 as a reducing agent. Now, the hydrogen transfer proceeds by an uninhibited radical chain mechanism with anthracenyl radicals as the chain carriers. For the kinetic analysis, the C–X (X = Br, Cl) bond dissociation enthalpies (*BDE*s) have been determined by means of very low pressure pyrolysis to give *BDE*(C–Br) = 271 kJ mol^{-1} and, as a lower limit, *BDE*(C–Cl) ≈ 309 kJ mol^{-1}, at 298 K. The *BDE*s are quite at variance with recently published insights derived from an electrochemical study. For comparison, density functional theory calculations (DFT) have been performed.

Introduction

The photocleavage of aromatic ketones present in lignin is of interest to understand the pivotal steps in the yellowing of pulp and paper.[1] Structural elements such as phenoxyl radicals.
and render phenacyl and phenoxyl radicals; subsequent (radical) reactions lead to the formation of undesired chromophores. Beside the β-photo cleavage,[1b] the excited aromatic ketone can be converted into a ketyl radical through hydrogen abstraction from the chemical environment.[1a] Recently, it has been shown that the elimination of a phenoxyl radical from this intermediate is quite slow at room temperature, due to a high activation barrier.[1a] Thermally, the same ketyl radical can be generated at elevated temperatures by means of reverse radical disproportionation (RRD, see Scheme 1).



Scheme 1. Reduction of α-X-acetophenones by RRD

Over the past years, we and others[2] have investigated the reactivity of various substituted naphthalenes and quinones in hydrogen-donating solvents, such as 9,10-dihydroanthracene (AnH_2). Both reduction and hydrodesubstitution have been reported. With 1-acetylnaphthalene for example, complete reduction of the side chain to yield 1-ethylnaphthalene can be achieved, whereas with 1-chloronaphthalene, formation of naphthalene takes place.[2a] The reduction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to the phenolic form already occurs at 350 K.[2b] The hydrogen shuttling involves the transfer of a hydrogen atom from a donor molecule to the oxygen atom of the carbonyl group as the rate-determining step. Since aromatic ketones are present in the lignin matrix, this chemical concept may find an application in the thermal liquefaction. Once the ketyl radical is formed at high temperatures, the elimination of the phenoxyl moiety is sufficiently fast and ultimately, the three-dimensional chemical network of lignin is ruptured into smaller, more useful feedstock compounds.

Alternatively, electron transfer has been proposed to be rate-determining for the reduction of quinones and phenacyl halogen compounds by NADH and model compounds.[3] Moreover, it has been noticed that in polar solvents, such as 2-propanol, even at room temperature α-bromo esters can be reduced by the ketyl radical derived from the alcoholic solvent by means of an electron-transfer pathway.[4] By way of contrast, in the same solvent, but at elevated temperatures (aromatic) ketones are reduced through hydrogen atom transfer.[5]

The photochemical conversion of α-haloacetophenones has been investigated by Scaiano and co-workers.[6] Both a radical chain mechanism and an electron-transfer mechanism have been observed, depending on the aromatic substituents and the applied solvent.

In this study, we report on the reactivity of phenacyl derivatives in the liquid phase, in the presence of various (hydrogen-donating) solvents between 373 and 573 K. Since both RRD and an electron-transfer mechanism can be anticipated, we embarked on a study employing various α- and ring-substituted acetophenones, including α-chloro- and α-bromoacetophenone. Furthermore, accurate knowledge of bond strengths is of crucial importance in mechanistic considerations and thus, gas-phase experiments have

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been carried out to determine the phenacyl−halogen bond dissociation enthalpies (*BDE*s). The toluene-carrier technique, as well as very low pressure pyrolysis (VLPP) have been used; both are versatile methods for bond-strength determinations.[7] Remarkably, only one, electrochemical determination for the *BDE*(C−Br) of phenacyl bromide has been published thus far, yielding a value for *BDE*(C−Br) of 197 kJ mol^{-1}.[8] This value seems to be at variance with group-increment rules, predicting 267 kJ mol^{-1}.[9]

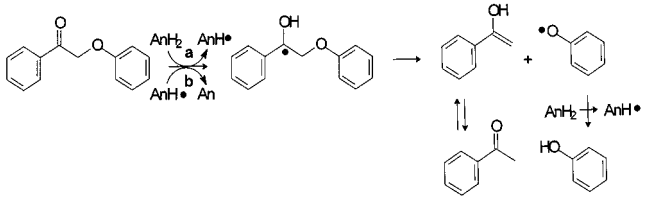
For comparison, the *BDE*s of interest have been calculated by the density functional theory (DFT) method.

Results

α-Phenoxyacetophenone in 9,10-Dihydroanthracene

In the presence of 0.9 M 9,10-dihydroanthracene (AnH_2) as the hydrogen donor, α-phenoxyacetophenone (PAP, 0.45 M in diphenyl ether as an inert diluent) was transformed into equal amounts of phenol and acetophenone (AP) with traces of benzaldehyde (selectivity < 5%) as the only side product. For every mole of converted PAP, one mol of anthracene (An) was obtained. Between 493 and 573 K, the conversion of PAP increased from 1% to 37%. Kinetically, this can be rationalized by a reverse radical disproportionation mechanism (RRD, Scheme 2, route **a**). The rate constant for the RRD is governed by the reaction enthalpy and with a pre-exponential factor of $10^{9.2}$ m^{-1} s^{-1},[10] the activation energy (E_a) was calculated from the rate of disappearance of PAP[14] and yielded E_a = 141 ± 4 kJ mol^{-1} (between 493 and 573 K). Taking into account the experimental uncertainties, this result is in range with the predicted value of 154 kJ mol^{-1}.[10]

Under the applied conditions, the cleavage of the ketyl radical is fast compared to the hydrogen abstraction from AnH_2.[2a] Subsequently, the phenoxyl radical is transferred to phenol by hydrogen abstraction. Acetophenone is obtained after the ketonization of the formed enol (Scheme 2).



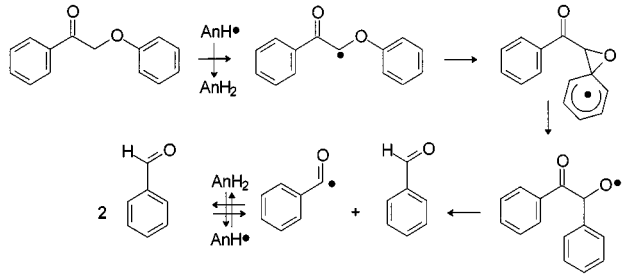
Scheme 2. Cleavage of PAP by RRD and by RHT

When a small amount of 7*H*-benz[*de*]anthracene (AnH_2/BzH = 15:1) was present, the conversion of PAP increased and ranged from 3% to 87% between 493 and 573 K. The enhanced PAP degradation rate is in accordance with the RRD mechanism: BzH is a better hydrogen donor than AnH_2 due to its lower *BDE*(C−H) and, as a result, a lower E_a for the RRD is obtained.[2b,15] BzH is regenerated by hydrogen abstraction from AnH_2 by the formed benzanthryl radicals (Bz•). Indeed, a complete recovery of BzH was observed together with An yields equimolar to the amount of converted PAP.

Competition experiments at 523 and 548 K in a mixture of AnH_2 and BzH (15:1) in diphenyl ether with α-phenoxyacetophenone and 2,4-dimethoxy-α-phenoxyacetophenone (DMPAP), showed that both compounds were converted at equal rates and product selectivities. The RRD reaction enthalpies for transfer of a hydrogen atom to the carbonyl group of PAP and derivatives should be independent of the aromatic substituents. As has been shown before, in benzyl bromides and *tert*-butylbenzenes, the effect of ring substitution on the benzylic stabilization enthalpy is negligible.[16] Hence, the thermal conversions of PAP and derivatives in AnH_2 follow an RRD mechanism. These experiments can be employed for the selective generation of (substituted) phenoxyl radicals.

The effect of added anthracene was studied by dissolving PAP (0.33 M) and equal amounts of AnH_2 and An (0.4 M each) in diphenyl ether. As a result, the conversion increased and at the same time more benzaldehyde was formed. For these reaction systems, the anthracenyl concentration is not only determined by the equilibrium AnH_2 + An ⇌ 2 AnH•, but also by species abstracting a hydrogen atom from AnH_2. When [AnH•] is sufficiently high, a second reduction pathway gains in importance: radical hydrogen transfer (RHT, Scheme 2, route **b**). Note that, in contrast with RRD, RHT follows a radical chain mechanism.

The experiments with PAP yielded benzaldehyde, which did not originate from the product acetophenone since added *p*-chloroacetophenone appeared to be inert. Hence, benzaldehyde formation most likely starts with the hydrogen abstraction from the CH_2 moiety of PAP by AnH•, according to Scheme 3, followed by rearrangement and cleavage of the alkoxyl radical. Indeed, with 2,4-dimethoxy-α-phenoxyacetophenone, equal amounts of benzaldehyde and 2,4-dimethoxybenzaldehyde were obtained. The relative rates for hydrogen shuttling between the CH_2 moiety and AnH• was further investigated by applying deuterated PAP (containing a CD_2 moiety) as the substrate. After 1 h at 572 K, the deuterium content in the remaining PAP decreased from 77% to 21%. From the product distribution it could be derived that the deuterium-hydrogen exchange is about three times faster than the cleavage of PAP. The fact that only a small amount of PAP is actually converted into benzaldehyde, demonstrates that the hydrogen abstraction from the CH_2 moiety in PAP (see Scheme 3) is reversible.



Scheme 3. Formation of benzaldehyde from PAP

To our surprise, addition of small amounts of α-bromoacetophenone (BrAP) to the reaction mixture accelerated the cleavage of PAP about 70 times at 514 K. In the next section, the fate of the α-haloacetophenones is described in more detail.

α-Bromo- and α-Chloroacetophenones in AnH_2

In AnH_2, already at 423 K quantitative reduction of α-bromoacetophenone (BrAP) to acetophenone and HBr was observed (see Table 1). At the same temperature, PAP was still inert. Ethylbenzene, the result of complete hydrogenation of the acetyl moiety of BrAP, was found as a side product and gained in importance at more elevated temperatures and higher AnH_2 concentrations (e.g. at 511 K, 1% in 0.8 M AnH_2 and 68% in 5 M). α-Chloroacetophenone (ClAP) reacted somewhat slower compared to BrAP. In most experiments with the halogen-containing acetophenones the mass balance was incomplete (see Table 1).

Table 1. Yields (%) of acetophenone (AP) and remaining phenacyl derivatives (α-XAP), in AnH_2 after 1 h

X	*T* [K]	XAP	AP	ethylbenzene
Br[a]	373	100	0	0
Br[a]	422	0	87[b]	< 1
Br[a] + 26% TEMPO	422	87	3	0
Br[a] + 6% DNB	422	0	99	< 1
Br[a]	480	0	90[c]	< 1
Br[a]	511	0	28	1
Cl[a]	516	75	12	0
Br[d]	390	95	5	0
Br[d]	405	45	36	1
Br[d] + 100% phenol	405	76	20	0
Br[d]	426	0	27	16
Br[d] + 100% phenol	426	5	77	2
Br[d]	475	0	< 1	45
Br[d]	512	0	< 1	68

[a] XAP (0.4 M) and AnH_2 (0.8 M) in diphenyl ether. – [b] The HBr yield was determined by titration and amounted to 74%. – [c] HBr yield 82%. – [d] XAP (0.2 M) in AnH_2 (5 M).

According to an RRD and an RHT mechanism, PAP, BrAP, and ClAP should react at equal rates. Hence, it seems that another mechanism holds for the phenacyl halides. Bond homolysis can be excluded since the *BDE*(C–Br) and *BDE*(C–Cl) are too high (vide infra). From the literature it is known that anthracenyl radicals can act as electron-donating species.[17] However, addition of 6% *m*-dinitrobenzene, a known inhibitor in electron-transfer processes,[3b] did not affect the conversion of BrAP. Since the reduction potentials of substituted acetophenones depend on the *para*-substituent,[18] competition experiments were performed of BrAP together with *p*-methoxy-, *p*-cyano-, and *p*-trifluoromethyl-α-bromoacetophenone. The conversions and product selectivities did not show any significant changes. Hence, electron transfer as the rate-determining step could be ruled out.

In contrast, the radical trap 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), inhibited the reduction (from 100% to 3% at 423 K), suggesting the presence of a radical chain process. Under these conditions TEMPO was converted for about 85%, mainly into 2,2,6,6-tetramethylpiperidine. α-(2,2,6,6-Tetramethylpiperidinyl)acetophenone was identified as a minor product. Radicals may recombine or disproportionate with TEMPO. Recombination with $AnH^{\bullet}$ is highly reversible, but disproportionation to yield anthracene and the hydroxylamine will be sufficiently fast. The hydroxylamine is subsequently reduced into the amine by an ionic mechanism.[19] Furthermore, the conversion decreased (e.g. from 55% to 24% at 405 K) upon addition of an equimolar (on BrAP) amount of phenol (a radical chain inhibitor). Both observations show that BrAP is converted by anthracenyl radicals (RHT). Thus, the difference between the behavior of PAP and that of BrAP may be due to differences in concentrations of $AnH^{\bullet}$.

α-Phenoxyacetophenone in Alcoholic Solvents

In 2-propanol as well as in cyclohexanol reduction of the oxo moiety of PAP to 2-phenyl-2-phenoxyethanol (PPE) was observed (e.g. 84% after 6 h at 500 K). Only small amounts of the cleavage products, phenol and acetophenone, were found (see Table 2). Addition of an equimolar amount of HBr led to an increased yield of the cleavage products; the PPE yield was not affected. In the product mixture of PAP with added HBr, a small amount of BrAP was observed, suggesting that PAP may first be transformed by HBr into BrAP and phenol (the reverse reaction has been applied for the synthesis of PAP).[21] Subsequently, BrAP is completely converted into acetophenone at these temperatures. It was shown that, under the applied conditions, acetophenone is a stable product in the presence of 2-propanol and HBr, indicating that BrAP cannot be formed from a reaction between acetophenone and HBr. However, after prolonged heating about 25% is hydrogen-

Table 2. Yields (%) of products and remaining phenacyl derivatives (α-XAP, 0.12 M) in alcohols after 1 h

X	solvent	*T* [K]	XAP	AP[a]	PPE[b]	high-boiling products[c]
PhO	2-propanol	500	96		4	
PhO	2-propanol[d]	500	16		84	
PhO	cyclohexanol	475	94	4	2	
PhO	cyclohexanol	556	37	7	56	
Br	2-propanol	426	44	31		22
Br	2-propanol + 26% TEMPO	426	42	28		33
Br	2-propanol	426	39	32		30
Br	2-propanol	475	4	48		41
Br	2-propanol	516	3	51		24
Br	cyclohexanol	475	0	97		0
Cl	2-propanol	475	90	4		10
Cl	2-propanol	516	75	10		10
Cl	cyclohexanol	475	83	10		2

[a] AP = acetophenone. – [b] PPE = 2-phenoxy-2-phenylethanol. – [c] Mass balances higher than 100% arise from errors in response factors for the high-boiling products, which were estimated from the number of carbon atoms as derived from the mass spectrum (from the M + 1/M ratio for the molecular ion peak). – [d] Reaction time = 6 h.

ated into 1-phenylethanol. Hence, the reduction of acetophenone is slower than that of PAP. In *sec*-butyl methyl ether, PAP was completely stable, even after prolonged heating.

α-Bromo- and α-Chloroacetophenones in Alcoholic Solvents

When 2-propanol was used as the solvent, the conversion of BrAP increased from 56% at 426 K to 96% at 475 K (see Table 2). In general, about half of the reacted BrAP was returned as acetophenone, the remaining part was transformed into products of which the exact structure could not be identified. Based on the m/z = 105 or 107 intensity in the individual MS spectra, substituted acetophenone and phenylethanol are suggested. In contrast to PAP, no hydrogenation of the carbonyl moiety to a hydroxy group was observed, because the conversion towards AP proceeds at considerably lower temperatures. The conversion of ClAP was considerably lower compared to that of BrAP. Addition of HBr to ClAP increased the conversion of the latter compound, probably due to halogen exchange (comparable to PAP, vide supra).[21]

Upon changing from 2-propanol to cyclohexanol, only a slight increase in the conversion was observed for both phenacyl halides accompanied by a substantial increase in selectivity towards acetophenone. A solvent-derived product was bromocyclohexane, indicative for addition of hydrogen bromide to cyclohexene. The latter compound is formed by acid-catalyzed dehydration of cyclohexanol.[22]

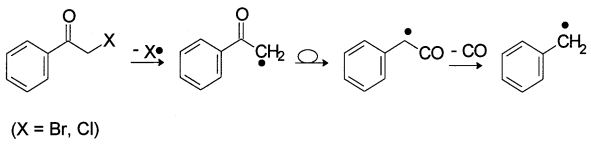
To disentangle the mechanism for the conversion of the phenacyl halides in alcoholic solvents, similar experiments were performed as when the solvent was AnH_2. Again, the distribution of the substituted acetophenones from competition experiments of BrAP with *p*-methoxy-, *p*-cyano-, and *p*-trifluoromethyl-α-bromoacetophenone did not show any substituent effect. Since the addition of *m*-dinitrobenzene also did not influence the BrAP conversion, it was concluded that also in this case, electron transfer does not take place. Unfortunately, an attempt to investigate the presence of a radical chain mechanism by addition of TEMPO did not succeed; TEMPO was converted for more than 90% into 2,2,6,6-tetramethylpiperidine and 2,2,6,6-tetramethylpiperidinol (product ratio 1/1.5),[19] but the conversion of BrAP remained at the same level.

Toluene-Carrier Gas-Phase Experiments with α-Bromo- and α-Chloroacetophenone

To determine the *BDE*(C−X) of BrAP and ClAP two methods were applied: a toluene-carrier technique and very low pressure pyrolysis (VLPP, see next section).

With the toluene-carrier method, a mixture of both compounds (about $3\cdot10^{-6}$ M BrAP and $6\cdot10^{-8}$ M ClAP) was thermolyzed at atmospheric pressure in nitrogen, using a large excess of *p*-fluorotoluene as the radical scavenger. The decay of both compounds and the yield of the major products (toluene, benzene, carbon monoxide, acetophenone, 4-fluorobibenzyl, and 1,3-diphenylpropanone), as a function of the temperature are shown in Figure 1. Only traces (≤ 1%) of other, unidentifiable products were observed. The overall aromatic ring balance decreased from 100% to 80% between 766 and 863 K. Other products stemmed from *p*-fluorotoluene, mainly 4,4′-difluorobibenzyl and fluorobenzene.

One remarkable fact can be noticed immediately: The difference in the rate of disappearance between BrAP and ClAP is quite modest, while based on a pure homolysis mechanism, a clear difference is expected since the carbon−bromine bond is much weaker than the carbon−chlorine bond (vide infra). Homolysis of the phenacyl halides leads to phenacyl radicals which, at these temperatures, rearrange and subsequently fragment into CO and benzyl radicals (Scheme 4). The rate of rearrangement is much faster than a bimolecular hydrogen transfer to give acetophenone. For example, the rate constant k_{rearr} at 810 K amounts to ca. 10^7 s^{-1},[23] while $k_{H\text{-}transfer} \times$ [toluene] = 26 s^{-1}.[26] Thus, toluene, CO, and 4-fluorobibenzyl (from the recombination of *p*-fluorobenzyl and benzyl radicals) can be identified as products stemming from the homolytic cleavage reaction. The other products, such as benzene and acetophenone, originate from one or more induced decomposition pathways. Based on the product composition, the contribution of the homolytic decomposition to the overall conversion increases with temperature from 35% to 56% between 766 and 863 K.



Scheme 4. Thermal homolytic decomposition of α-X-acetophenones

In view of the strong C−Cl bond in ClAP, no bond homolysis can be expected and the conversion of ClAP is entirely governed by an induced process. Accepting that the overall rates for induced decomposition of ClAP and BrAP are equal, the difference between the experimental pseudo-first-order rate constants for both compounds, $k_{BrAP} - k_{ClAP}$, should give the rate constant for the homolytic conversion of BrAP. From these experiments it can be deduced that $k_{BrAP,\ homolysis}$ [s^{-1}] = 2.0×10^{15} exp(−263 [kJ mol^{-1}]/*RT*), nicely correlating with the VLPP results (vide infra).

The induced decomposition of BrAP and ClAP most likely involves hydrogen atom chemistry (wall-mediated reactions can be excluded since the increase of the surface/volume ratio of the reactor by a factor of 6.5 did not change the product distribution). Hydrogen atoms are formed in side reactions next to the recombination of fluorobenzyl radicals. These radicals do not quantitatively yield 4,4′-difluorobibenzyl, but also render high-boiling compounds (up to soot) and hydrogen atoms.[29] Thus, addition of a hydrogen atom to the *ipso* position of the aromatic ring of BrAP produces benzene, ketene, and a halogen atom

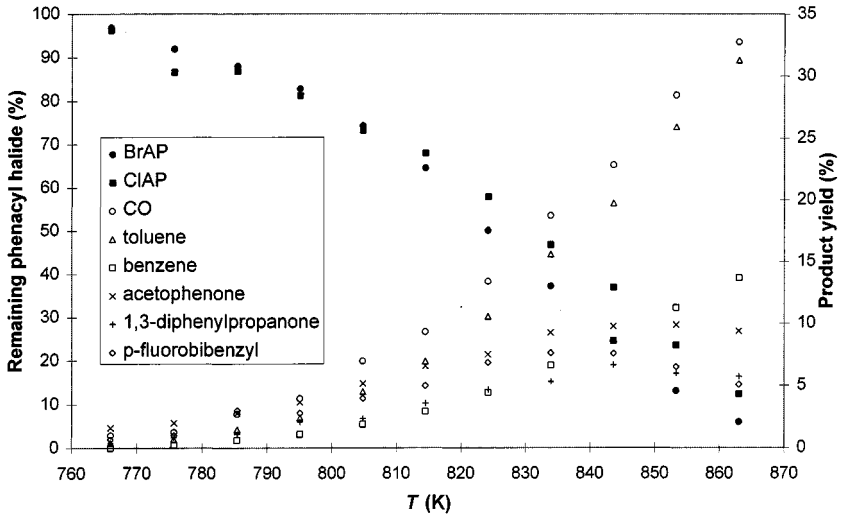
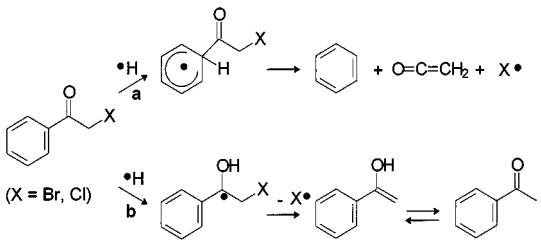


Figure 1. Thermolysis of ClAP and BrAP in *p*-fluorotoluene: decay of substrates and yields of main products (relative to the intake of BrAP)

(Scheme 5, route **a**),[30] while hydrogen atom addition to the carbonyl group leads to acetophenone (Scheme 5, route **b**). From the benzene yield, a hydrogen atom concentration of around 10^{-10} M can be derived,[31] which is not unlikely for these type of gas-phase experiments.[32]



Scheme 5. Hydrogen atom induced decomposition of a α-X-acetophenones

The interaction of hydrogen atoms was further explored by using deuterated toluene (average deuteration of the methyl substituent: 65%) as the radical scavenger. With a reaction mixture consisting of α-bromoacetophenone, *p*-chloroacetophenone, and deuterated toluene, it appeared that at ca. 50% conversion of BrAP, the degree of deuterium incorporation in the product acetophenone (55% [D_1], 17% [D_2], 2% [D_3]) was higher than that in *p*-chloroacetophenone (24% [D_1], 3% [D_2]). No deuterium was found to be incorporated in the aromatic ring of the acetophenones. The hydrogen−deuterium exchange in *p*-chloroacetophenone cannot take place by hydrogen abstraction from the α-carbon atom by deuterated benzyl radicals since the *p*-chlorophenacyl radical, once formed, will be converted into *p*-chlorobenzyl radicals, according to step 2 and 3 in Scheme 4.

The observed higher incorporation of deuterium in the product acetophenone is the consequence of deuterium atom addition to the carbonyl group of BrAP (Scheme 5, route **b**). For BrAP, the addition is directly followed by the fast elimination of the halogen atom, yielding the enol form of acetophenone. The direct rearrangement of this [D_1]enol into acetophenone has an activation energy of 310 kJ mol^{-1},[33] and is too slow. The enol is ketonized by the catalytic action of DBr,[34] formed after deuterium abstraction from the carrier by bromine atoms. As a result, the produced acetophenone contains one deuterium atom. The deuterium atom addition takes place for all acetophenones present. The lower deuterium incorporation for *p*-chloroacetophenone indicates that the exchange is under kinetic control: The rate for the reverse reaction of α-unsubstituted acetophenone is comparable to that for the elimination of a hydrogen atom to yield the enol. Part of the deuterium incorporation may also arise through the direct keto−enol equilibration, catalyzed by DBr. Indeed, the unreacted BrAP also contained a small amount of deuterium (16% [D_1], 2% [D_2]).

1,3-Diphenyl-1-propanone, a byproduct in the experiments with BrAP and *p*-fluorotoluene, is most likely formed after addition of a benzyl radical to the double bond of the enol form of BrAP, followed by elimination of the bromine atom, and hence is a probe for the existence of the enol in the gas phase. Addition to the enol of the product acetophenone is also possible, but since no leaving group is present, only the reverse reaction takes place once the adduct is formed.

Gas-Phase Experiments with α-Bromo- and α-Chloroacetophenones at Very Low Pressure

The decomposition of BrAP starts at 800 K and is complete at around 1150 K, as was found by monitoring the decay of the molecular ion *m*/*z* = 198. At the same time, an increase was observed for *m*/*z* = 91 and 92 (benzyl and toluene) as well as for *m*/*z* = 79, 80, 81, and 82 (bromine atoms and hydrogen bromide), and *m*/*z* = 28 (carbon monoxide). As has been described before,[7a] radical species that are formed inside the reaction vessel are partially transformed by (wall-associated) hydrogen-transfer reactions into molecules. Small amounts of benzene (*m*/*z* = 77, 78)

and acetophenone (m/z = 105) were also observed. The combined yields of $Br^{\bullet}$ + HBr as well as those of $PhCH_3$ + $PhCH_2^{\bullet}$ increased linearly with the BrAP conversion over the entire temperature range, in accordance with the homolysis mechanism for BrAP (Scheme 4). Rearrangement and subsequent CO elimination from the phenacyl radical is fast and quantitatively renders benzyl and toluene.[24,35]

The conversion of ClAP started at around 1000 K and increased to 80% at 1173 K. The chlorine yield (i.e. $Cl^{\bullet}$ + HCl) linearly increased with the conversion, indicating that ClAP quantitatively yields chlorine atoms. Similar products as for BrAP were observed, albeit with a much larger phenyl yield. Based on the ratio m/z = (77 + 78):(91 + 92), the contribution of the phenyl to the total aromatic product yield increased from 35% to 90% between 1000 and 1200 K (< 10% for BrAP). Clearly, a different decomposition pathway is present. Based on the product spectra it seems that a complete recovery of the aromatic rings as well as the halogen content is accompanied by a loss of the CH_2 moiety.

Two alternative mechanisms can be put forward for the decomposition of ClAP (because of the low pressure, any induced decomposition pathway can be excluded). Firstly, cleavage of the carbonyl−chloromethyl bond followed by CO elimination from the benzoyl radical. However, the chloromethyl radicals should appear as chloromethane while only a minor increase in m/z = 49−52 was observed. Moreover, based on standard group increment rules and density functional theory calculations (vide infra), this bond is stronger than the carbon−chlorine bond. The second option is a 1,1-elimination of HCl, followed by rupture into phenyl, CO, and methylidene (CH). The latter species may not be detectable. For comparison, the decomposition of 1,3-dichloroacetone was investigated (conversion at 1173 K: ca. 57%, somewhat lower than ClAP) and a similar product pattern was found: chlorine atoms, hydrogen chloride, and carbon monoxide. No significant amounts of methyl chloride or ketene were observed and therefore the 1,1-elimination of HCl seems the prevailing mechanism in this case and also for ClAP. Thus, for the pyrolysis of ClAP, the measured activation energy (vide infra) only renders the lower limit for the *BDE*(C−Cl).

From the decrease in the abundance of the molecular ions, the rate constants were calculated for BrAP and ClAP. The vibration frequencies necessary for the RRKM algorithm (see Experimental Section) were computed by the density functional theory method (vide infra). Since only one of the Arrhenius parameters can be derived some of the low frequencies of the ground state vibrational model were adjusted to yield a pre-exponential factor $A = 10^{15.3}$ s^{-1}.[36] The Arrhenius equations were found as k_{BrAP} [s^{-1}] = $10^{15.3}$ exp(−258 [kJ mol^{-1}]/RT) and k_{ClAP} [s^{-1}] = $10^{15.3}$ exp(−296 [kJ mol^{-1}]/RT), assuming that in both cases the carbon−halogen bond is cleaved. However, only for BrAP, the measured activation energy actually resembles the *BDE*(C−X). By use of the DFT-calculated C_p value, the bond strength at 298 K is obtained: *BDE*(C−Br) = 271 kJ mol^{-1}.[37] This value is somewhat higher than the one calculated by density functional theory, 253 kJ mol^{-1} (vide infra). When the same procedure is followed for ClAP, a lower limit for the *BDE*(C−Cl) = 309 kJ mol^{-1} is obtained.

Our values for the *BDE*s in the phenacyl halides (271 and 309 kJ mol^{-1} for C−Br and C−Cl, respectively) are close to the predicted values[9][38] and comparable to those for the benzyl halides (254 and 285 kJ mol^{-1}),[16,39] but deviate substantially from the bond strengths reported by Savéant et al. (198 and 232 kJ mol^{-1}).[8] The VLPP method we applied allows straightforward measurements of bond strengths. Savéant et al. measured the reduction potentials of the phenacyl halides by cyclic voltammetry to derive the bond strengths. Clearly, application of that method, as well as the interpretations, should be reconsidered, at least for this type of compounds.

Density Functional Theory Calculations

The computations for BrAP and ClAP resulted in minimal energy structures where all carbon, oxygen, and halogen atoms were situated in one plane. In the case of the phenacyl radical the complete structure is almost flat. Based on the calculated electronic energies and zero-point vibrational energies, the reaction enthalpies were computed (see Table 3). In order to derive the accuracy of the used method some C−X bond dissociation enthalpies were calculated and compared with experimental values, reported in the literature. From Table 3, it can be concluded that even for small molecules, the theoretically derived *BDE*s do not match the experimentally obtained values. For chloromethane and chloroethane, the deviation even increased when a larger basis set was chosen.

Table 3. Bond strengths at 298 K [kJ mol^{-1}] in compounds of interest as calculated by DFT

compound	experimental	6-31G(d)	6-311+G(d,p)
CH_3−Br	295[a]	305	285
CH_3−Cl	349[a]	337	326
CH_3CH_2−Cl	354[a]	334	327[b]
$PhC(O)CH_2$−Br	271[c]	253	
$PhC(O)CH_2$−Br		248[d]	
$PhC(O)CH_2$−Cl	309[e]	282	
$PhC(O)CH_2$−Cl		301[d]	
PhC(O)−CH_2Cl		305	
$PhC(O)CH_2$−H	396[f]	391	

[a] Ref.[13] − [b] Calculated using the 6-311G(d,p) basis set.[41] −[c] Measured by VLPP, this work. − [d] Derived from the isodesmic reaction XAP + CH_4 → AP + CH_3X, using *BDE*(C−H) in CH_4 = 439 kJ mol^{-1},[28] *BDE*(C−Br) in CH_3Br = 295 kJ mol^{-1},[13] *BDE*(C−Cl) in CH_3Cl = 349 kJ mol^{-1},[13] and *BDE*(C−H) in acetophenone = 396 kJ mol^{-1} (see note[f]). − [e] Lower limit, based on the conversion of ClAP measured by VLPP (this work). − [f] Equal to the *BDE*(C−H) in acetaldehyde.[13]

The values calculated from isodesmic reactions (in which the total number of each type of bond before and after the reaction is the same) are generally believed to be more reliable.[42] For BrAP, the calculated *BDE* deviates about 20 kJ mol^{-1} from the experimental value. Since the calculated

value for the *BDE*(C−H) in acetophenone is quite comparable with the measured value, it can be concluded that the deviation in bond strengths for the phenacyl halides is mainly caused by the erroneous handling of the halogen atoms by DFT.

We also calculated the *BDE* for the carbonyl−chloromethyl bond in ClAP. According to the DFT calculations, the difference between *BDE*(PhCOCH$_2$−Cl) and *BDE*(PhCO−CH$_2$Cl) is about 23 kJ mol^{-1}.

Discussion

Two reaction pathways can be mentioned for the reduction of the α-halogen-substituted acetophenones in 2-propanol and AnH$_2$: a hydrogen-transfer mechanism (RRD or RHT) and an electron-transfer mechanism. Conclusive evidence for the first pathway appears from the experiments with the *para*-substituted α-bromoacetophenones: No significant influence of the substituent was observed. Both Renaud et al.[6a,43] and Andersen et al.[18] have shown that a large difference in rate constants can be expected for an electron-transfer process, due to the difference in reduction potentials of the substrates. Since addition of both TEMPO and phenol decreased the BrAP conversion in AnH$_2$, the conclusion can be drawn that a radical chain mechanism (RHT) is present with anthracenyl as the chain carrier (comparable to route **b** in Scheme 2). The same holds for the reduction of BrAP in 2-propanol, where the 2-hydroxy-2-propyl radical is the chain carrier.

The primary product acetophenone is formed in the enol form.[44] The subsequent ketonization takes place by HBr catalysis. In AnH$_2$, this reaction is not extremely fast and in competition with the complete side chain reduction resulting in ethylbenzene, especially at higher temperatures.[45]

Since the rates of formation of the ketyl radical are the same in all cases, the differences in reactivity and product distribution between the α-substituted acetophenones can be explained by considering the rates of conversion of the ketyl radicals. The predominant decomposition pathway for the ketyl radical is the elimination of the α-substituent of which the rate will be different for the various ketyl radicals. With bromine at the α-position, a rate constant of 10^3 s^{-1} can be derived in AnH$_2$ at 422 K.[47] Other reactions such as hydrogen abstraction from the solvent or disproportionation with AnH$^\bullet$ are too slow (8 s^{-1},[54] and 10 s^{-1},[55] respectively) to compete with the bromine elimination. At 422 K, the decomposition of BrAP is just complete and thus $k_{overall} > 10^{-3}$ s^{-1}, which is equal to k_{RHT} [AnH$^\bullet$]. From $k_{RHT} \approx 10^5$ m^{-1} s^{-1},[56] it follows that [AnH$^\bullet$] $\approx 10^{-8}$ M.

In the case of ClAP, the elimination of a chlorine atom from the ketyl radical is much slower ($2\cdot10^{-2}$ s^{-1})[47] and disproportionation with AnH$^\bullet$ or hydrogen abstraction from AnH$_2$ are the main reactions. Since only traces of 1-phenylethanol were observed, the first option prevails and as a result, ClAP is reformed and the concentration of AnH$^\bullet$ decreases.

The rate for elimination of phenoxyl from the ketyl radical is also 10^3 s^{-1},[47] which would suggest comparable conversions for both BrAP and PAP. The fact that PAP is inert at low temperatures where BrAP is already reduced, is the result of the difference in reactivity between the product radicals: phenoxyl and the bromine atom. Abstraction of a hydrogen from AnH$_2$ by the bromine atom is an exothermal (−48 kJ mol^{-1})[58] process and regenerates the chain carrier (anthracenyl). When a phenoxyl radical is formed, although the exothermicity is the same,[58] the hydrogen abstraction rate appears to be much slower. Thus, radical disproportionation with the anthracenyl radical becomes a competitive process and the concentration of AnH$^\bullet$ will decrease. As a consequence, phenoxyl radicals act as radical-chain terminating species and the cleavage of PAP can only occur at temperatures where hydrogen abstraction from the hydrogen-donor solvent becomes feasible. Under those conditions, the reduction of PAP in AnH$_2$ proceeds by reverse radical disproportionation (RRD) while radical hydrogen transfer (RHT) will gain in importance with increasing temperature.

Similar considerations hold for the reduction reactions in alcoholic solvents. It should be noted that, due to the stronger C−H bond, RRD is not feasible. Hence, direct transfer of a hydrogen atom follows a mechanism with the 2-hydroxy-2-propyl radical as the chain carrier. The RHT process now pertains to the shuttling of a hydrogen atom from one oxygen center to another oxygen center (see Scheme 2). These reactions have been documented quite well in photochemical studies.[57] The difference in the rate of conversion for BrAP between AnH$_2$ and 2-propanol may be due to the lower rate for the regeneration of the chain carrier (hydrogen abstraction from 2-propanol is now endothermal and becomes rate determining). Also, the product selectivity is different: next to acetophenone, other (high-boiling) compounds emerge. Since the exact structure of these products could not be established, we refrain from speculations as to the pathway(s) of formation.

PAP can be expected to be inert in 2-propanol. Indeed, only small amounts of cleavage products (phenol and acetophenone) were observed. Instead, the slow reduction of the carbonyl to the alcohol (PPE) was observed at 500 K (see Table 2). Since PAP is stable in *sec*-butyl methyl ether, it can be suggested that a concerted 1,2-hydrogen transfer from the alcohol to PAP renders PPE. The lower PPE yield in cyclohexanol will most likely be caused by increased steric hindrance in this concerted hydrogen transfer. At much higher temperatures, it has been shown that the reduction of aromatic ketones follows a radical chain pathway.[5] If indeed there is a change in mechanism with the temperature, this may be caused by the fact that the hydrogen transfer becomes irreversible. The hydrogen abstraction from the solvent by the intermediate ketyl radical, derived from the aromatic ketone, is now fast enough to sustain a radical chain.

Experimental Section

Liquid-Phase Experiments: The procedure has been described in detail before.[46] In short, a pyrex tube of ca. 2 ml was charged for

about one third with 10^{-4} mol of substrate, 0.6 ml of solvent, and naphthalene as an internal standard. Prior to sealing the tubes under vacuum in liquid nitrogen, the air was replaced by helium in three freeze-pump-thaw cycles. After heating in a furnace, the tube was cooled down rapidly and decapped. Then, the reaction mixture was dissolved in toluene or acetone and *n*-dodecane was added as an external standard. The analyses were performed with 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 CP-Sil-5-CB column and helium as the carrier gas.

Gas-Phase Experiments: Experiments at atmospheric pressure were performed using a device as described before,[59] with nitrogen as the bath gas. *p*-Fluorotoluene (ca. $5\cdot10^{-4}$ M) was used as a radical scavenger and methane as an injection standard. Residence times were between 3.5 and 4.5 s. The substrates and *p*-fluorotoluene were introduced separately by evaporation with nitrogen as the carrier gas. − The apparatus for the very low pressure pyrolysis experiments has been described before.[7a] α-Chloroacetophenone (ClAP) was introduced by evaporation at room temperature, α-bromoacetophenone (BrAP) at 333 K. A medium ionization energy of 45 eV was selected to obtain a relatively high abundance for the molecular ion but to avoid a large degree of fragmentation of the reagent and the products. The initial substrate concentration (intensity of the molecular ion) was derived from blank runs at low temperatures. The combined product mass spectrum was retrieved after correction for the fragmentation of the starting compound. The rate constants according to unimolecular decay were calculated and the Arrhenius expression at infinite pressure was obtained by use of the RRKM algorithm.[7a,60]

Computational Procedures: Density functional theory (DFT) calculations were performed using Gaussian 94W rev. E.3[61] using a PC equipped with a Pentium 200 MHz processor and 32 MB RAM memory. The B3LYP functionals on the 6-31G(d) basis set were employed for both the geometry optimization and the frequency calculations. This basis set was chosen to obtain optimum results with respect to both the accuracy and the calculation time. It took 169 h to optimize the geometry of BrAP and to calculate the frequencies. The same procedure for the phenacyl radical required 292 h of computation time. The calculated vibrational frequencies were corrected by a factor of 0.97 to compensate for the anharmonicity.[62]

Chemicals: α-Phenoxyacetophenone (PAP) was synthesized from BrAP and phenol: A solution of 0.05 mol of α-bromoacetophenone in 30 ml of acetone was added dropwise to a stirred mixture of 0.06 mol of phenol and 0.06 mol of K_2CO_3 in 50 ml of acetone. After stirring during 48 h at room temperature, acetone was evaporated and dichloromethane added. The organic layer was washed twice with 125 ml of a 5% NaOH solution and dried with $MgSO_4$, followed by evaporation of the CH_2Cl_2. The obtained solid was crystallized three times from boiling ethanol. PAP was collected as white crystals with a GC purity of 99.8%. The same method was used for synthesis of 2,4-dimethoxy-α-phenoxyacetophenone, starting with α-bromo-2,4-dimethoxyacetophenone and phenol. − Deuterated PAP (Ph−CO−CD_2−O−Ph) was obtained after refluxing 0.4 g of PAP for 18 h in a mixture of 0.4 g of NaOH, 80 ml of dioxane, and 6 ml of D_2O. After neutralization with HCl and extraction with ether, the combined extracts were washed with water and dried with $MgSO_4$. After evaporation of the solvent, recrystallization from ethanol resulted in 0.16 g of product, consisting of 56% [D_2] PAP, 42% [D_1] PAP, and 2% [D_0] PAP (by GC-MS analysis). − α-Bromo-*p*-trifluoromethylacetophenone was synthesized by a procedure based on that reported by King and Ostrum.[63] During 15 min, a solution of 3 g of *p*-trifluoromethylacetophenone (Aldrich, 98%) in 10 ml of chloroform was added under nitrogen to a stirred, refluxing solution of 7.2 g of ground copper(II) bromide in 10 ml of ethyl acetate. After an additional 45 min of refluxing under nitrogen, the solution was filtered, the solvents were evaporated and the remaining red solid material was crystallized from boiling toluene. The desired product was obtained as white crystals with a GC purity of 94%. − 7*H*-Benz[*de*]anthracene (94%), α-bromo-*p*-cyanoacetophenone (Lancaster, 97%), and other compounds (Aldrich, highest purity) were used as received. Anthracene (Aldrich, > 95%) was mixed with boiling methanol and the hot solution decanted. 9,10-Dihydroanthracene (Janssen, 97%) was recrystallized from methanol before use. For the very low pressure experiments, BrAP and ClAP were purified by sublimation. Nitrogen (Air Products, 99.999%) was passed through an oxygen filter before use.

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[15] Using the *BDE*(C−H) in BzH of 276 kJ mol^{-1},[12] $\Delta_r H$ becomes 112 kJ mol^{-1} and the rate equation $k_{RRD,BzH}$ [M^{-1} s^{-1}] = $10^{8.9}$ exp(−112 [kJ mol^{-1}]/RT).[10] Hence at 573 K, $k_{RRD,BzH}$ = $3\cdot10^3$ × $k_{RRD,AnH2}$.
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[45] The first step is the reduction of the double bond in the enol with the ketyl radical as an intermediate. The product, 1-phenylethanol contains a benzylic hydroxy group which is very susceptible towards protonation and subsequent water elimination.[46] The formed cation can be transferred into ethylbenzene by hydride transfer from the solvent,[46] or eliminate a proton yielding styrene. Polymerization of styrene is very fast at the applied temperatures and may render a low mass balance.
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[47] Since the addition of a halogen atom to an olefine proceeds nearly activationless,[25] we approximate that E_a ≈ $\Delta_r H$. For elimination of a phenoxyl radical, E_a ≈ $\Delta_r H$ + 25 kJ mol^{-1}.[49] With A = 10^{13} s^{-1} and $\Delta_r H$ from ref.[50], the rate for the elimination of X$^\bullet$ from the ketyl radical at 422 K becomes $4\cdot10^{-13}$ s^{-1} (X = H), $2\cdot10^{-2}$ s^{-1} (X = Cl), and $1\cdot10^3$ s^{-1} (X = Br, PhO). In the case of aliphatic systems the rate for elimination of Br$^\bullet$ is much faster than that of PhO$^\bullet$, at room temperature.[48] For example, for $XC_2H_4^\bullet \rightarrow X^\bullet + C_2H_4$ a difference in $\Delta_r H$ of 18 kJ mol^{-1} can be estimated between X = PhO$^\bullet$ and X = Br$^\bullet$.[13] Using the additional activation barrier of 25 kJ mol^{-1} for phenoxyl, a difference in E_a of 7 kJ mol^{-1} is estimated. This is not in agreement with the experimental observations,[48] thus the barrier of 25 kJ mol^{-1}, which has been derived from the addition of phenoxyl to styrene, may well be higher for aliphatic systems.
[48] P. Mulder, unpublished results.
[49] J. T. Autrey, M. S. Alnajjar, D. A. Nelson, J. A. Franz, *J. Org. Chem.* **1991**, *56*, 2197.
[50] For XAP, $\Delta_r H$ for the elimination of the X from the ketyl radical (XAPH$^\bullet$) can be derived as 80 kJ mol^{-1} (X = Br), 118 kJ mol^{-1} (X = Cl), 56 kJ mol^{-1} (X = PhO), and 205 kJ mol^{-1} (X = H), using $\Delta_f H$ of XAPH$^\bullet$ and X$^\bullet$ atoms from refs.[51][52], $\Delta_f H$ of the enol isomer of acetophenone as −46 kJ mol^{-1},[53] and $\Delta_f H$(PhO$^\bullet$) = 52 kJ mol^{-1}.[36]
[51] The addition of a hydrogen atom to the carbonyl group in the phenacyl derivatives is an exothermal process ($\Delta_r H$ = −164 kJ mol^{-1}),[10] and independent of the α-substituent. Hence, using $\Delta_f H$(H$^\bullet$) = 218 kJ mol^{-1},[13] $\Delta_f H$(AP) = −87 kJ mol^{-1},[13] $\Delta_f H$(BrAP) = −68 kJ mol^{-1},[52] and $\Delta_f H$(ClAP) = −97 kJ mol^{-1},[52] the formation enthalpies for the ketyl radicals (XAPH$^\bullet$) can be derived as −14 kJ mol^{-1} (X = Br), −43 kJ mol^{-1} (X = Cl), and −33 kJ mol^{-1} (X = H). When (X = PhO), $\Delta_f H$ = −50 kJ mol^{-1}.[1a]
[52] $\Delta_f H$(XAP) = $\Delta_f H$(AP$^\bullet$) + $\Delta_f H$(X$^\bullet$) − *BDE*(C−X) with *BDE*(C−X) as the measured values from Table 3, $\Delta_f H$(Br$^\bullet$) = 112 kJ mol^{-1},[13] $\Delta_f H$(Cl$^\bullet$) = 121 kJ mol^{-1},[13] and $\Delta_f H$(AP$^\bullet$) = 91 kJ mol^{-1}, as derived from the *BDE*(C−H) (taken equal to that in acetaldehyde, 396 kJ mol^{-1})[13], $\Delta_f H$(H$^\bullet$) = 218 kJ mol^{-1},[13] and $\Delta_f H$(AP) = −87 kJ mol^{-1}.
[53] Ref.[33], p. 90.
[54] Hydrogen abstraction from AnH_2 by the ketyl XAPH$^\bullet$ is independent of X, with E_a = 67 + 0.35 × $\Delta_r H$ kJ mol^{-1} and A = $10^{8.6}$ m^{-1} s^{-1}.[11] For X = PhO: $\Delta_f H$(PAPH$^\bullet$) = −50 kJ mol^{-1} and $\Delta_f H$(PAPH$_2$) = −163 kJ mol^{-1}.[1a] With $\Delta_f H$(H$^\bullet$) = 218 kJ mol^{-1},[13] the benzylic *BDE*(C−H) in PAPH$_2$ is 331 kJ mol^{-1}. With a *BDE*(C−H) in AnH_2 of 318 kJ mol^{-1},[12] E_a = 62 kJ mol^{-1} and k[AnH$_2$] = 8 s^{-1}.
[55] In general, for the disproportionation k = 10^9 M^{-1} s^{-1}, [AnH$^\bullet$] will be ca. 10^{-8} M (see text).

[56] At 298, $k_{RHT} = 10^3$ M^{-1} s^{-1},[57] and using $A = 10^8$ M^{-1} s^{-1}, it follows that $E_a = 25$ kJ mol^{-1} and thus at 422 K, $k_{RHT} \approx 10^5$ M^{-1} s^{-1}.
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[58] *BDE*(H−Br) = 366 kJ mol^{-1},[28] *BDE*(C−H) = 318 kJ mol^{-1} in AnH_2,[12] and *BDE*(O−H) = 366 kJ mol^{-1}.[36]
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