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# The Reactivity of *o*-Hydroxybenzyl Alcohol and Derivatives in Solution at Elevated Temperatures

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The reactivity of *o*-hydroxybenzyl alcohol (*o*-HBA, **1**), as a model compound for lignin, has been studied in various solvents between 390 and 560 K. Both in polar and apolar solvents the benzylic cation is the reactive intermediate. In alcoholic solvents, the benzylic cation reacts with the solvent to give the corresponding ethers. Relative reaction rates have been determined for different alcohols; a factor of 14 is encountered between the most (methanol) and least (*tert*-butyl alcohol) reactive ones. The etherification is reversible, in contrast to the electrophilic aromatic substitution with phenol and anisole, for which $k_{\mathrm{PhOH}} = 1 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{\mathrm{anisole}} = 1 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, at 424 K. In apolar hydroaromatic solvents, 7*H*-benz[*de*]anthracene, 9,10-dihydroanthracene, and 9,10-dihydrophenanthrene, the formation of *o*-cresol proceeds via hydride transfer from the solvent to the benzylic cation; rate constants at 555 K are $2 \times 10^6$, $5 \times 10^4$, and $5 \times 10^3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively.

## Introduction

During the past decades, the demand for alternative sources of chemical feedstock has increased due to a growing awareness of the depletion of crude oil reserves. The utilization of woody biomass as a renewable source is therefore an appealing option. Lignin, for example, may be converted into (substituted) phenols. Liquid-phase hydrocracking, in the presence of hydroaromatic solvents such as tetralin, seems to be a promising route for the degradation of lignin into monoaromatic products.[1] Furthermore, alcohols, 1,4-dioxane, and water can be used in processing lignin or model compounds.[2]

Quinone methides (QMs) have been suggested as important intermediates in the photochemical and thermal chemistry of lignin.[3] However, only a limited number of studies detail the dynamic behavior of *o*-quinone methide (*o*-QM). *o*-Hydroxybenzyl alcohol (*o*-HBA, **1**) has been reported as a precursor for *o*-QM[4] and can also be considered as a model compound for structural elements in lignin: 5% of the aromatic units in lignin contain a benzylic hydroxyl moiety.[5] Moreover, during lignin processing *o*-methoxyphenolic units are partially converted into *o*-HBA derivatives.[6]

In the photosolvolysis of *o*-HBA, under alkaline and neutral conditions, Wan et al.[7] have proposed the formation of *o*-QM via intramolecular proton transfer. In the presence of methanol, *o*-QM is converted into the corresponding methyl ether (**2**). The existence of *o*-QM has been further substantiated on the basis of product studies in the presence of nucleophiles or dienophiles. However, the observed products can be equally well explained by an ionic pathway in which the benzylic cation is the reactive intermediate. A nanosecond laser flash photolysis study of a neutral aqueous solution of *o*-HBA and derivatives has revealed a long-lived species that, according to its lifetime (>5 s) and the absorption spectrum, was identified as *o*-QM. If the intermediate were a benzylic cation, the lifetime would have been less than 1 μs.[8] During photocondensation of *o*-HBA in alkaline media the formation of oligomers has been reported,[9] which may or may not proceed via *o*-QM. Similar oligomers have been observed in the acid-catalyzed formation of Bakelite resins; in that case the benzylic cation acts as the intermediate.[10]

Previously, we have identified *o*-QM directly with on-line mass spectrometric analysis in the gas phase at low pressure by thermal treatment of *o*-HBA and chroman.[4a] At atmospheric pressures, this intermediate appears to be extremely reactive and rapid oligomerization occurs, even under dilute conditions.[4b] In the presence of toluene as a hydrogen source, *o*-QM

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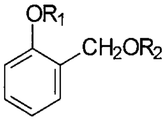
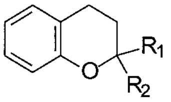
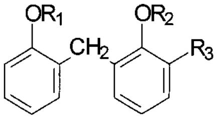
**Chart 1**



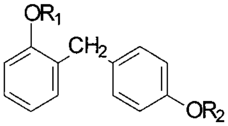
| | | | |
|---|---|---|---|
| **1** | $R_1 = H$ | $R_2 = H$ | *o*-hydroxybenzyl alcohol (*o*-HBA) |
| **2** | $R_1 = H$ | $R_2 = CH_3$ | *o*-(methoxymethyl)phenol (*o*-MMP) |
| **3** | $R_1 = CH_3$ | $R_2 = H$ | *o*-methoxybenzyl alcohol (*o*-MBA) |
| **4** | $R_1 = H$ | $R_2 = C_2H_5$ | *o*-(ethoxymethyl)phenol |
| **5** | $R_1 = H$ | $R_2 = 2\text{-}C_3H_7$ | *o*-(2-propoxymethyl)phenol (*o*-PMP) |
| **6** | $R_1 = H$ | $R_2 = tert\text{-}C_4H_9$ | *o*-(*tert*-butoxymethyl)phenol |
| **7** | $R_1 = H$ | $R_2 = CH_2(C_6H_5)$ | 2-hydroxydibenzyl ether |
| **8** | $R_1 = CH_3$ | $R_2 = 2\text{-}C_3H_7$ | *o*-(2-propoxymethyl)anisole |



| | | | |
|---|---|---|---|
| **9** | $R_1 = CH_3$ | $R_2 = CH_3$ | 2,2-dimethylchroman |
| **10** | $R_1 = H$ | $R_2 = OC_2H_5$ | 2-ethoxychroman |

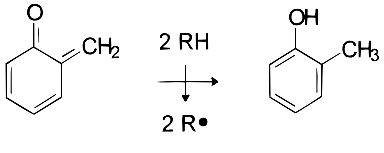


| | | | | |
|---|---|---|---|---|
| **11** | $R_1 = H$ | $R_2 = H$ | $R_3 = H$ | 2,2'-dihydroxydiphenylmethane (2,2'-DHD) |
| **12** | $R_1 = H$ | $R_2 = CH_3$ | $R_3 = H$ | 2-hydroxy-2'-methoxydiphenylmethane (2,2'-HMD) |
| **13** | $R_1 = CH_3$ | $R_2 = CH_3$ | $R_3 = H$ | 2,2'-dimethoxydiphenylmethane (2,2'-DMD) |
| **14** | $R_1 = H$ | $R_2 = H$ | $R_3 = CH_2OH$ | 2,2'-dihydroxy-3-(hydroxymethyl)diphenylmethane |



| | | | |
|---|---|---|---|
| **15** | $R_1 = H$ | $R_2 = H$ | 2,4'-dihydroxydiphenylmethane (2,4'-DHD) |
| **16** | $R_1 = H$ | $R_2 = CH_3$ | 2-hydroxy-4'-methoxydiphenylmethane (2,4'-HMD) |
| **17** | $R_1 = CH_3$ | $R_2 = CH_3$ | 2,4'-dimethoxydiphenylmethane (2,4'-DMD) |

can be transformed into *o*-cresol in two steps: a reverse radical disproportionation mechanism (RRD, see eq 1) followed by hydrogen abstraction.[4b] Hence, the *o*-cresol formation can be directly related to the presence of *o*-QM.



(1)

This report deals with the behavior of *o*-HBA, as a lignin model compound, under thermal liquefaction conditions. For comparison, the reactivities of some benzylic alcohol derivatives have been explored as well. Hydroaromatic and alcoholic solvents have been used, in a temperature range of 390−560 K, to investigate whether quinone methide chemistry is relevant under thermal, solution-phase conditions (Chart 1).

## Experimental Section

The liquid-phase experiments were carried out in sealed Pyrex tubes (ca. 1.5 mL). After the tube was filled approximately one-third with the reagents and an internal standard (naphthalene), the air was removed by three freeze-pump-helium-thaw cycles. Subsequently, the tube was sealed under vacuum (ca. 400 Pa) and placed in a thermostat-controlled oven. The temperatures applied were reached within 5 min. After the thermal treatment the reaction chamber was cooled to room temperature (in about 5 min), and toluene or acetone and an external standard (*n*-dodecane) were added. For calculation of the initial concentration, the amount of *o*-HBA weighed into the tube was corrected for the amount of GC-identifiable impurities (5%) consisting of *o*-cresol and *o*-hydroxybenzaldehyde. However, during the course of the experiments it was noticed that the results varied depending on the purity of *o*-HBA. These differences could not be explained by the presence of *o*-cresol and *o*-hydroxybenzaldehyde but may arise due to small amounts of an acid, most likely *o*-hydroxybenzoic acid. However, proper detection by GC analysis was not possible.[11]

The samples were analyzed in quadruplicate on an HP 5890 GC (column: CPsil 5 CB) equipped with hydrogen as the carrier gas and an FID detector. For identification of unknown products an HP 5972 mass selective detector was used. Response factors for available compounds were calculated by injecting mixtures of known composition. For compounds not available, response factors were estimated on the basis of the number of carbon and oxygen atoms and related to similar, available chemicals. $^1$H NMR spectra of 200 scans in acetone-$d_6$ were performed on a 300 MHz DPX300 apparatus from Bruker. IR spectra were measured on a Unicam SP3-200 double beam infrared spectrometer.

**Chemicals.** *o*-(Methoxymethyl)phenol (*o*-MMP, **2**) was prepared according to a synthesis reported previously[12] and further purified by aqueous phase extraction (final purity 96%). All other reagents were obtained in the purest grade and used as received, except for 9,10-dihydroanthracene, which was crystallized twice from methanol (GC purity >99%). *o*-HBA was used as such, and a purified batch (>99%) was prepared as well by means of sublimation or recrystallization from a 1/9 toluene/*n*-hexane mixture.

## Results

***o*-HBA in Hydroaromatic Solvents.** The chemistry of *o*-hydroxybenzyl alcohol (*o*-HBA, **1**, 0.07 M) was studied in mixtures of 9,10-dihydroanthracene ($AnH_2$, 3.3 M) and 7*H*-benz[*de*]anthracene (BzH, 0.3 M), where BzH acts as the hydrogen donor and is regenerated via hydrogen abstraction from $AnH_2$ by the $Bz^•$ radical.[1] The conversion of *o*-HBA was complete after 1 h at temperatures above 475 K. *o*-Cresol emerged as a product and the yield gradually increased with temperature, up to a maximum of 88% at 555 K. In these experiments no conversion of BzH was observed and about equimolar amounts of anthracene were formed with respect to *o*-cresol. At 555 K, the *o*-cresol yield was independent of the reaction time (0.75−2 h); this reaction product was shown to be stable under the applied conditions. By diluting the hydrogen-donor mixture with (inert) diphenyl ether (DPE), it was found that the *o*-cresol yield increased linearly with the BzH concentration.

Particularly at low reaction temperatures, an incomplete mass balance was obtained. No products other than *o*-cresol could be detected besides traces (≤2%) of a high-boiling compound. On the basis of GC and GC−MS analysis, this material was identified as a (condensation) dimer of *o*-HBA (**14**). Presumably, the dimer is indicative for the formation of other oligomers (which could not be detected) and may account for the low mass balance. With *o*-HBA heated (for 1 h at 474 K) in inert solvents (diphenyl ether and 1,4-dioxane) a precipitate could be isolated and characterized as diphenylmethane derivatives.[13] When the oligomer was heated in 9,10-dihydroanthracene at 555 K for 1 h, only coalification took place.

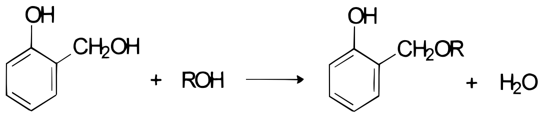
The nature of the applied hydroaromatic solvent was varied: at 555 K, starting with 0.18 M *o*-HBA, the *o*-cresol yield amounted to 5% in 9,10-dihydrophenanthrene ($PhenH_2$, 4.8 M), 34% in $AnH_2$ (4.7 M), and 84% in a mixture of BzH (1.3 M) and $AnH_2$ (3.3 M). Thus, relative rate constants for the *o*-cresol formation at 555 K can be derived as $k_{PhenH2}/k_{AnH2}/k_{BzH} = 1/10/340$.[14] With purified *o*-HBA similar results were obtained, although a somewhat lower reactivity at temperatures below 500 K was noticed accompanied by a somewhat higher selectivity toward *o*-cresol.

**Table 1. Product Distribution (%)[a] of Reactions with *o*-HBA (0.22 M) in Various Solvents at 424 K**

| solvent | *o*-HBA[b] | ether[c] | *o*-cresol[c] | other[c,d] |
|---|---|---|---|---|
| methanol | 5 | 94 | < 1 | 0 |
| ethanol | 21 | 78 | 0 | < 1 |
| 2-propanol | 35 | 65 | 0 | 0 |
| *tert*-butyl alcohol | 47 | 52 | 0 | < 1 |
| cyclohexanol | 29 | 62 | < 1 | 0 |
| benzyl alcohol | 18 | 82 | 0 | 0 |
| diphenyl ether | 62 | | 0 | 8[e] |
| 1,4-dioxane | 33 | | 0 | < 1 |
| acetonitrile | 82 | | 0 | 1 |
| $AnH_2$[f] | 68 | | 0 | 2 |
| $AnH_2$/BzH 10/1[f] | 40 | | 2 | 0 |

[a] Average of four analyses, accuracy ± 1%, reaction time 1 h. [b] Recovered substrate: $(100\%\{[o\text{-HBA}]_t/[o\text{-HBA}]_{t=0}\})$. [c] Detected products: $(100\%\{[\text{product}]_t/[o\text{-HBA}]_{t=0}\})$. [d] High boiling products. Based on GC−MS analysis, 60−100% of these products was the dimer **14**. No other products could be identified. [e] Of which 7% aromatic substitution products (ortho/para = 1/6). [f] Initial *o*-HBA concentration 0.07 M.

***o*-HBA in Alcoholic Solvents.** In alcoholic solvents (methanol, ethanol, 2-propanol, *tert*-butyl alcohol, and benzyl alcohol) at relatively low temperatures, *o*-HBA was converted with a high selectivity (e.g., 95% in methanol after 1 h at 424 K) into the corresponding ethers (**2**, **4**, **5**, **6**, and **7**, see Table 1), according to eq 2.



(2)

Only above 500 K did the total mass balance decrease. The *o*-HBA purity did not affect the reaction rates or selectivities. Two other benzylic alcohols that were applied under the same conditions, benzyl alcohol and *o*-methoxybenzyl alcohol (*o*-MBA, **3**), appeared to be almost inert.

With *o*-(methoxymethyl)phenol (*o*-MMP, **2**) dissolved in 2-propanol or *tert*-butyl alcohol, an ether/alcohol interchange was observed. Hence, under the applied conditions the ether formation is reversible. The conversion of *o*-MMP, another precursor for *o*-QM,[15] in 2-propanol at 424 K (22%) is lower in comparison with that of

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(11) On the basis of the response factor of separately synthesized *o*-MMP and after correction for the observed amounts of *o*-cresol and *o*-hydroxybenzaldehyde as impurities in *o*-HBA, a complete mass balance was obtained in the experiments with *o*-HBA in methanol. Hence, the amount of acid impurities in *o*-HBA, most likely *o*-hydroxybenzoic acid, is less than 1%. Further quantification is not possible in view of the strong interaction of benzoic acids with the applied GC column. It should be noted that the presence of small amounts of acid may well be important for the overall solution's acidity. For with 0.22 M *o*-HBA (together with 1% of *o*-hydroxybenzoic acid) dissolved in phenol (10 M) and using the $pK_a$ values of around 4 and 10, respectively, the acidity is still dictated by the organic acid.

(12) De Jonge, J.; Bibo, B. H. *Rec. Trav. Chim. Pays-Bas* **1955**, *74*, 1448−1452.

(13) The precipitates from diphenyl ether and 1,4-dioxane were analyzed by $^1$H NMR and IR spectroscopy and shown to be identical. In the IR spectrum absorptions were visible at 3100−3700 (s), 2900 (w), 1600 (w), 1500 (s), 1450 (m), 1250 (s), 1100 (w), and 750 (w) cm$^{-1}$. The $^1$H NMR spectrum showed two broad signals at $\delta = 3.6-4.0$ and 6.6−7.3 ppm, which were assigned to the methylene and aromatic protons, respectively, of the oligomeric structure. In addition, three broad phenolic resonances were observed in the region 7.9−8.6 ppm. Because of the absence of the characteristic carbonyl frequencies (e.g., strong band at 1650−1720 cm$^{-1}$) in the IR spectrum, an oligomer of *o*-QM could be excluded. Both the IR and $^1$H NMR spectra are in good accordance with those reported by Wan from Bakelite resins produced in the photocondensation of *o*-HBA in an alkaline medium.[9]

(14) By using $[o\text{-cresol}]_{t=1h}/[\text{oligomer}]_{t=1h}$ equals $(k_{PhenH2} \times [PhenH_2]_{t=0})/(r_{olig})$ in $PhenH_2$, $(k_{AnH2} \times [AnH_2]_{t=0})/(r_{olig})$ in $AnH_2$, and $\{(k_{BzH} \times [BzH]_{t=0}) + (k_{AnH2} \times [AnH_2]_{t=0})\}/(r_{olig})$ in BzH and assuming equal rates for the oligomerization ($r_{olig}$).

*o*-HBA (61%). Apparently, the elimination of methanol is somewhat slower than that of water.

From Table 1, a distinct difference in the rate of *o*-HBA conversion at 424 K can be noticed when applying different alcoholic solvents: methanol > benzyl alcohol ≈ ethanol > cyclohexanol > 2-propanol > *tert*-butyl alcohol. To determine the rate of decomposition ($k_{\mathrm{decomp}}$) the decay of *o*-HBA in 2-propanol was followed in time ($t = 0-90$ min) at this temperature, using an initial substrate concentration of 0.20 M. With a forced mass balance consisting of the remaining *o*-HBA and formed *o*-(2-propoxymethyl)phenol (*o*-PMP, **5**) ($[o\text{-HBA}]_{t=0} = [o\text{-HBA}]_t + [o\text{-PMP}]_t$, which was close to the actual mass balance) a rate constant of $k_{\mathrm{decomp}} = 4.0 \times 10^{-4}\ \mathrm{s}^{-1}$ was obtained from the linear plot ($r^2 = 0.99$) of -ln($[\mathrm{HBA}]_t/[\mathrm{HBA}]_{t=0}$) vs reaction time. At a lower *o*-HBA concentration (0.005 M), $k_{\mathrm{decomp}} = 3.5 \times 10^{-4}\ \mathrm{s}^{-1}$ ($r^2 = 0.97$) was found, indicating first-order behavior.

The relative rate constants for ether formation with the various alcohols ($k_{\mathrm{ROH}}$), derived from competition experiments, revealed $k_{\mathrm{MeOH}}/k_{\mathrm{EtOH}}/k_{\mathrm{benzOH}}/k_{2\text{-PrOH}}/k_{t\text{-BuOH}} = 14/8/5/4/1$, independent of reaction time (1−4 h) and temperature (394−475 K). Ether formation can be envisaged by either *o*-QM or the benzylic cation as the intermediate reacting with the alcoholic solvent. The ratios in rate constants as we observed are quite similar to those found for the addition of the diphenylmethyl cation.[16]

In *tert*-butyl alcohol, the formation of (2,2-dimethylchroman, **9**) was observed as an additional product at 475 K. It is known that isobutene can be formed from *tert*-butyl alcohol at elevated temperatures in a slightly acidic environment.[18] Indeed, when the tube was opened, evolution of a volatile compound was visible. The mechanism of formation can be rationalized by a Diels−Alder addition of *o*-QM or the benzylic cation to isobutene. In alcohol mixtures including *tert*-butyl alcohol, the yield of 2,2-dimethylchroman (**9**) increased with time,[19] at the expense of the product ethers, although their ratios remained constant. Clearly, the formation of **9** is kinetically irreversible, in contrast to the ether formation. This also implies that both processes start with one common intermediate, and thus, ether formation through a direct $S_N2$ mechanism can be excluded.

Ethyl vinyl ether (EVE), a commonly used trap for *o*-QM[8] and benzylic cations,[17] was also applied to intercept the intermediate in the *o*-HBA thermolysis. In a mixture of EVE (0.3 M), methanol (3.0 M), and benzyl alcohol (4.8 M) at 424 K the *o*-HBA conversion was 77% (see Table 1). Ether derivatives from methanol (**2**) and benzyl alcohol (**7**) as well as 2-ethoxychroman (**10**) were found as products in a ratio of 40/28/9. At 475 K *o*-HBA is quantitatively converted into **10**. On the basis of the product yields at 424 K it can be approximated that $k_{\mathrm{EVE}}/k_{\mathrm{MeOH}} = 2$ and $k_{\mathrm{EVE}}/k_{\mathrm{benzOH}} = 5$. These relative reactivities toward EVE can be regarded as upper limits, since the ether formation is already reversible under these conditions. For comparison, $k_{\mathrm{EVE}}/k_{\mathrm{MeOH}}$ is around 0.1 for (diphenylmethyl) cations at 298 K.[17]

**Table 2. Product Distribution (%)[a] of Reactions with *o*-HBA (0.22M) in (Mixtures of) Phenol and Anisole at 424 K**

| solvent[b] | *o*-HBA[c] | ether | 2,2′-DHD[d] ***2,2′-HMD*** | 2,4′-DHD[d] ***2,4′-HMD*** | other[d,e] |
|---|---|---|---|---|---|
| phenol | <1 |  | 50 | 31 | 4 |
| anisole | 68 |  | ***3*** | ***10*** | <1 |
| 2-propanol/phenol 1/1 | 5 | 70 | 10 | 7 | 2 |
| 2-propanol/anisole 1/1 | 56 | 42 | <***1*** | <***1*** | <1 |
| anisole/phenol 1/1 | 23 |  | 34 | 17 | 8 |
|  |  |  | ***1*** | ***3*** |  |

[a] Average of four analyses, accuracy ± 1%, reaction time 1 h. [b] Solvent ratio in M/M. [c] Recovered *o*-HBA: ($100\%\{[o\text{-HBA}]_t/[o\text{-HBA}]_{t=0}\}$). [d] Detected products: ($100\%\{[\text{product}]_t/[o\text{-HBA}]_{t=0}\}$). [e] High boiling product, mainly **14**.

***o*-HBA in Phenol and Anisole.** To explore the option of the benzylic cation as intermediate, phenol was used as a solvent (Table 2), being a very potent trap for carbocations. When *o*-HBA was heated in neat phenol, two major products were observed with high selectivities: 2,2′- and 2,4′-dihydroxydiphenylmethane (2,2′- and 2,4′-DHD, **11** and **15**).[20] The same products (**11**, **15**) were obtained with *o*-MMP, whereas *o*-methoxybenzyl alcohol (*o*-MBA, **3**) was almost inert. Ether formation between *o*-HBA and phenol did not take place. The products can only be explained to arise from electrophilic aromatic substitution of the benzylic cation at the ortho and para positions of the aromatic ring. The third isomer, stemming from addition to the meta positions, could not be detected (detection limit: 0.5%). Very low yields of the meta isomer in the electrophilic substitution with activated monoaromatics have been reported before.[21] In phenol/alcohol mixtures, the ratio DHD/ether increased both with time and temperature. The formation of the ether from *o*-HBA with the alcohol is kinetically favored but reversible, in contrast to the aromatic substitution. The ortho/para ratio varied with temperature and cosolvent between 1 and 3. The higher preference for the ortho substitution has been documented quite well; the difference in isomer ratio between neat phenol and phenol mixed with another solvent may be caused by the variation in the hydrogen bonding of phenol.[21,22]

No significant changes were observed when purified *o*-HBA was applied, albeit that the ortho/para ratio increased to about 4.

Rates of aromatic substitution relative to ether formation were determined with *o*-HBA in mixtures of phenol and 2-propanol. By extrapolation to $t = 0$ of the plot of the ratio DHD/ether at 424 K vs time (which gave a linear relation), the ratio of $k_{\mathrm{PhOH}}/k_{2\text{-PrOH}}$ could be retrieved. Using the rate constant for addition of the benzylic cation to 2-propanol, $k_{2\text{-PrOH}} = 5 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 424 K,[23] the

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(15) (a) Gardner, P. D.; Sarrafizadeh R. H.; Brandon, R. L. *J. Am. Chem. Soc.* **1959**, *81*, 5515. (b) Cavitt, S. B.; Sarrafizadeh R. H.; Gardner, P. D. *J. Org. Chem.* **1962**, *27*, 1211−1216.

(16) Ratios $k_{\mathrm{MeOH}}/k_{\mathrm{EtOH}}/k_{2\text{-PrOH}}/k_{t\text{-BuOH}} = 17/12/4/1$ were found at 293 K in acetonitrile.[17]

(17) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710−7716.

(18) McMurry, J. *Organic Chemistry*, 2nd ed.; Brooks/Cole: Pacific Grove, 1988; p 596. *o*-HBA or acidic impurities can serve as the acid catalyst.

(19) Remarkably, next to 2,2-dimethylchroman (**9**), another, yet unknown product, was observed when *tert*-butyl alcohol was used as a solvent together with methanol, 2-propanol, and benzyl alcohol.

(20) In phenol, 2,2′- and 2,4′-DHD (**11** and **15**) are identified by comparison with spectra in the NIST GC−MS library. In anisole, 2,2′- and 2,4′-HMD (**12** and **16**) are identified based on GC (retention times) and GC−MS analysis.

(21) Harvey, D. R.; Norman, R. O. C. *J. Chem. Soc.* **1961**, 3604−3610.

(22) Watson, W. D. *J. Org. Chem.* **1974**, *39*, 1160−1164.

(23) The reaction rate of the benzylic cation with an alcohol is about $10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 295 K,[8, 24] and by applying a preexponential factor of $10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, an activational energy of 23 kJ mol$^{-1}$ is obtained. Thus, at 424 K, $k_{\mathrm{ROH}} = 5 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

rate constant for the electrophilic aromatic substitution with phenol was obtained: $k_{\mathrm{PhOH}} = 1 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$.

After 1 h at 475 K, *o*-MBA in a mixture of phenol and 2-propanol appeared to be inert. However, after addition of an equimolar amount of nonpurified *o*-HBA, *o*-MBA was converted for 23% with a 5% yield of **8** and 15% of the substitution products **13** and **17** (ortho/para = 1/1). Simultaneously, *o*-HBA was completely converted into **5** (10%), **11** (62%), and **15** (24%). Apparently, the phenol acidity is not sufficient enough to render a benzylic cation from *o*-MBA, which demonstrated that a (stronger) organic acid is present in nonpurified *o*-HBA.[11]

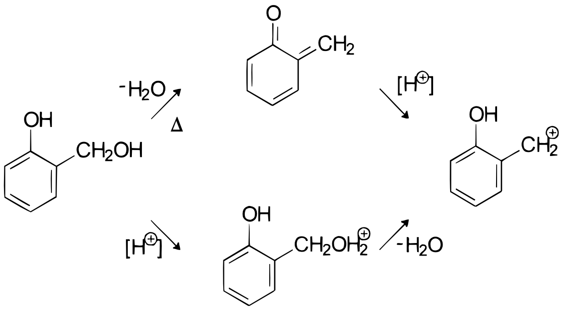
With unpurified *o*-HBA in anisol, similar substitution products were found: 2-hydroxy-2′-methoxydiphenylmethane and 2-hydroxy-4′-methoxydiphenylmethane (2,2′- and 2,4′-HMD, **12** and **16**).[20] The ortho/para ratio of ca. 0.32 in anisole tallies nicely with the ratio found for other electrophilic substitution reactions[21,25] and was independent of temperature and (alcoholic) cosolvents. By using a mixture of phenol and anisole, the former was found to be 10 times more reactive, and thus, $k_{\mathrm{anisole}} = 1 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ at 424 K. Surprisingly, in anisole the results did depend on the purity of the starting material. Upon purification the conversion decreased and only traces of aromatic substitution products were obtained. Oligomerization appears to be the major reaction pathway.

The relative reactivity of the cation toward either BzH and anisole was further investigated.[26] The product ratio *o*-cresol/HMD at 555 K linearly increased with the ratio BzH/anisole. This clearly indicates that both *o*-cresol and the aromatic substitution products are formed from the same precursor, the benzylic cation. From the slope, the ratio in rate constants $k_{\mathrm{BzH}}/k_{\mathrm{anisole}} = 11$ ($r^2 = 0.997$) was derived.[27]

## Discussion

***o*-HBA Degradation.** Two mechanisms can be advanced for the conversion of *o*-HBA in solution at elevated temperatures (Scheme 1): thermal, concerted elimination of water to yield *o*-QM and an acid-catalyzed dehydration to form a benzylic cation. From the obtained reaction products in various solvents: ethers (alcohols), aromatic substitution compounds (phenol, anisol), chroman derivatives (isobutene, ethyl vinyl ether), and *o*-cresol (hydroaromatic solvents) no real distinction can be made between the two routes. Moreover, the benzylic cation may also arise through rapid protonation of *o*-QM. From the competition experiments with various types of solvents it is, however, clear that the same intermediate is present in all cases.

**Scheme 1**



In anisole a strong dependence of the conversion and product spectrum exists on the solution's acidity. In the absence of protons, aromatic substitution does not occur, indicating that *o*-QM needs to be protonated first before such a reaction can take place. The main pathway for *o*-QM is now oligomerization. Our results show that phenol is a strong enough acid to protonate *o*-QM to produce the prerequisite intermediate for the aromatic substitution: the benzylic cation. On the other hand, *o*-MBA (due to the methyl group a direct elimination can be excluded) is almost inert in phenol as the solvent, indicating that the acidity is still too low to render the benzylic cation. Thus, the initial step in the thermal degradation of *o*-HBA seems to be direct formation of *o*-QM.

Conversely, the constant ratio of ether products from *o*-HBA in a mixture of alcohols over a range of 80 K may be an indication for the direct protonation mechanism for *o*-HBA decomposition at least in polar solvents. The variation in addition rates to different alcohols, which are quite similar to those advanced for benzylic cation reactivity,[17] may be explained by a steric effect:[7] with *tert*-butyl alcohol the lowest addition rate is found. Since this is an entropic contribution and probably only small differences in reaction enthalpies exist for the different alcohols, the individual rate constants will only slightly vary with the temperature. Moreover, at our reaction temperatures the ether formation is reversible. Therefore, the observation that the product spectrum does not change with time and temperature indicates that the ether decomposition also proceeds via an ionic mechanism. Otherwise, the rates for direct, concerted alcohol elimination from the ethers need to be almost identical to accommodate our observations, which seems unrealistic.

Thus, no decisive conclusion can be drawn from the current experiments as to the mechanism of the *o*-HBA thermolysis in the liquid phase, but it is certain that in all cases the benzylic cation acts as the reactive intermediate for product formation.

The rate of decomposition of *o*-HBA depends on the type of solvents, as can be seen in Table 1. An explanation can be found in the different degrees of hydrogen bond accepting capacities of the solvents. To semiquantify the role of intermolecular hydrogen bonding we used the solvent parameter $\beta_2^{\mathrm{H}}$, a commonly used parameter to quantify the contribution of hydrogen bonding.[28] In Figure 1, the plot is displayed of $\log(k_{\mathrm{decomp}})$ as a function of the solvent $\beta_2^{\mathrm{H}}$ for various solvents. For the alcoholic solvents, a fair correlation is obtained, not only for the neat solvents (including phenol) but also for mixtures

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(24) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373–1383.

(25) Norman, R. O. C.; Radda, G. K. *J. Chem. Soc.* **1961**, 3610–3616.

(26) In these experiments, the mass balance amounted to 43–47% of the initial *o*-HBA concentration. In all experiments ca. 2% of the dimer of *o*-HBA was found and ca. 3% of an unknown, high-boiling product.

(27) Assuming the same temperature dependence as in ref 23, $k_{\mathrm{anisole}} = 2 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$ at 555 K; thus, $k_{\mathrm{BzH}} = 2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$. Consequently, from $k_{\mathrm{PhenH2}}/k_{\mathrm{AnH2}}/k_{\mathrm{BzH}} = 1/10/340$ (see text): $k_{\mathrm{AnH2}} = 5 \times 10^4$ and $k_{\mathrm{PhenH2}} = 5 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$.

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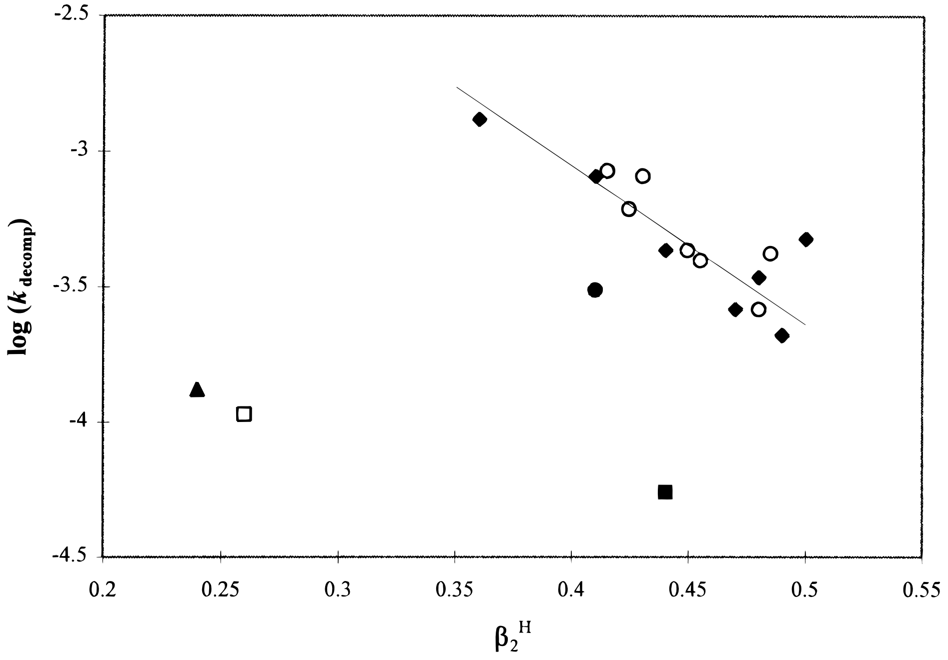


**Figure 1.** Correlation between log($k_{decomp}$) and $\beta_2^H$ for *o*-hydroxybenzyl alcohol conversion at 424 K in neat alcoholic solvents (◆), mixtures of alcohols (○), acetonitrile (■), 1,4-dioxane (●), anisole (□), and diphenyl ether (▲). Values for $\beta_2$H for the alcohols from ref 28c, for the other compounds from ref 28d.

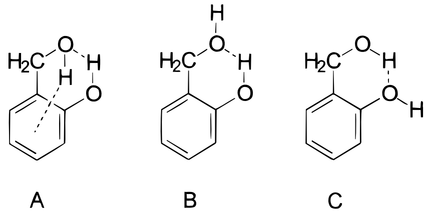
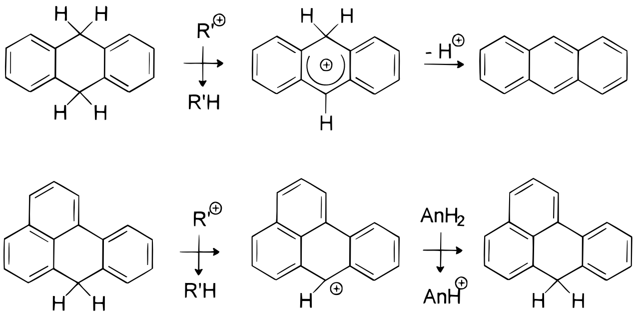


**Figure 2.** Conformations of *o*-hydroxybenzyl alcohol.

of these solvents, for which we used linearly averaged $\beta_2$H values. In the non-hydrogen-bonding solvent, carbon tetrachloride, three different intramolecular-hydrogen-bonded conformers of *o*-HBA have been identified by infrared spectroscopy at room temperature. The conformers A and B predominate (see Figure 2),[29] while type C only exists in small amounts. Apparently, when *o*-HBA is less intermolecularly bonded the elimination of water, most likely from the intramolecularly bonded conformer A, proceeds faster.

***o*-Cresol Formation.** In hydroaromatic solvents, a quantitative conversion of *o*-QM into *o*-cresol can be expected. The RRD of *o*-QM with the used hydrogen donors is sufficiently fast[4b] relative to other, nonionic processes. However, the *o*-cresol yield depends on both the hydrogen-donating capability of the solvent and on the hydrogen-donor concentration. Instead of the RRD mechanism, the formation of *o*-cresol involves the shuttling of a hydride ion from the solvent to the benzylic cation. Analogous hydride-transfer reactions from $AnH_2$ have been reported before.[30] After formation of the anthracenylic cation, anthracene is formed by a fast proton elimination[30a] (Scheme 2). In the case of the more reactive BzH, proton elimination from the carbocation is not feasible and BzH is recycled by hydride abstraction from $AnH_2$.

**Scheme 2**



The derived rate constants for hydride abstraction by the benzylic cation (e.g., $k_{AnH2} = 5 \times 10^4$ M$^{-1}$ s$^{-1}$) are in range with those published before for reaction of carbon cations with hydride donating compounds.[31] The formation of *o*-cresol by hydride transfer can be compared with the hydrogen atom transfer from the same donor solvents to the benzyl radical. In both cases, the reaction rate constants increase in the same order, $PhenH_2 < AnH_2 <$ BzH, and the derived ratios in rate constants are quite similar. Surprisingly, the absolute rate constants for hydride transfer[27] are larger than those for hydrogen atom transfer.[32] Thus, on the basis of dynamic studies only, it can be difficult to distinguish between both processes. More in general, the analogy between an ionic and radical pathway needs to be treated with great caution.[35]

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An analogeous conversion mechanism for benzylic alcohols may also be operative during the reduction of benzophenone to diphenylmethane in hydroaromatic solvents at more elevated temperatures, as has been performed by Choi and Stock.[36] Initially, the ketone is reduced to the benzhydrol, via radical chemistry (i.e., RRD followed by hydrogen abstraction). Subsequently, due to the sensitivity of the benzylic hydroxyl group toward acid-catalyzed dehydroxylation, a benzylic cation is formed as intermediate, $Ph_2C^+H$. As we have shown, such a cation can abstract a hydride from the hydroaromatic solvent, resulting in diphenylmethane. This rationale excludes the formation of an ether from the cation and benzhydrol as well as numerous other reactions that have been proposed to explain the observations.

## Final Remarks

On the basis of the results, we are convinced that the benzylic cation is the reactive intermediate in the thermal, liquid-phase degradation of *o*-HBA in the presence of a catalytic amount of acid. However, many results (but not all) can also be explained on the basis of *o*-QM as the intermediate. Experiments to distinguish *o*-QM and the benzylic cation by spectroscopic methods at these conditions could be helpful in solving this matter.[37]

In many approaches for isolating and converting lignin, polar solvents are applied. On the basis of the results in this paper, it can be concluded that, in the presence of small amounts of an acid, benzylic cations can be formed in the lignin matrix upon heating. A large number of acidic phenolic groups are present in lignin, and the polar solvent increases the proton mobility through the matrix. Next to ionic chemistry,[38] radical chemistry (e.g., hydrogen shuttling)[1] can take place as well, which increases the complexity of lignin degradation. Electrophilic aromatic substitution of the formed cationic moieties may be regarded as one of the steps in the unwanted coke formation during the processing of lignin.

**Acknowledgment.** The authors wish to thank Danilo Santoro for kindly supplying a sample of 7*H*-benz[*de*]anthracene.

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(32) For the reaction $PhCH_2^\bullet + RH \rightarrow PhCH_3 + R^\bullet$, the reaction enthalpies, $\Delta_r H$, can be calculated as −21, −54, and −100 kJ mol$^{-1}$, respectively, for RH = PhenH$_2$, AnH$_2$, and BzH.[33] The Arrhenius parameters can be derived according to the Evans−Polanyi relation:[34] $\log A = 8.0$ per H, $E_a = 67 + 0.35 \times \Delta_r H$ kJ mol$^{-1}$. At 555 K the rate constant for hydrogen abstraction by benzyl radicals from PhenH$_2$, AnH$_2$, and BzH can thus be calculated as $1 \times 10^3$, $1 \times 10^4$, and $2 \times 10^5$ M$^{-1}$ s$^{-1}$, respectively.

(33) By using differential functional theory (DFT) calculated values from: Santoro, D.; Korth, H. G.; Mulder, P. To be published.

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(37) The authors wish to thank an anonymous reviewer for insisting that our data are also consistent with *o*-QM reactivity.

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