o-Quinone methide as a common intermediate in the pyrolysis of *o*-hydroxybenzyl alcohol, chroman and 1,4-benzodioxin

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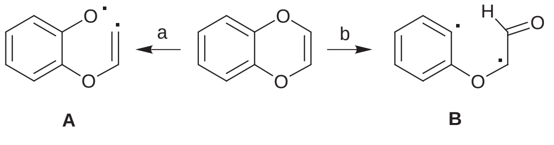
The product composition in the very low pressure pyrolysis (550–1210 K) of *o*-hydroxybenzyl alcohol (HBA), 3,4-dihydro-2*H*-1-benzopyran (chroman), and 1,4-benzodioxin (BD) indicates that *o*-quinone methide (*o*-QM) is the common intermediate in each case. At complete conversion of HBA, *o*-QM was observed as the only product and the mass spectrum of *o*-QM could be obtained. At higher temperatures (>950 K), *o*-QM is subsequently converted into benzene and CO. The thermolysis process for chroman starts with cleavage of the phenoxy–carbon bond and proceeds with ethene elimination, yielding *o*-QM. The high pressure rate parameters for unimolecular decay have been determined to obey $k_{\mathrm{chroman}}/\mathrm{s}^{-1} = 10^{15.3} \exp(-269/RT)$. For BD only the cleavage of the phenyl–vinoxy bond has been observed, and after rearrangement and CO elimination *o*-QM is formed. The Arrhenius equation for the overall rate of disappearance has been found as $k_{\mathrm{BD}}/\mathrm{s}^{-1} = 10^{15.6} \exp(-310/RT)$. Ultimately (1100 K) the thermolysis of BD leads to 1 mole of benzene and 2 moles of CO.

Introduction

Quinone methides are regarded as important reactive intermediates in the (photo)chemical conversion of lignin.[1] Recently, we have shown that *o*-quinone methide (*o*-QM, 6-methylenecyclohexa-2,4-diene-1-one) emerges as an intermediate in the thermolysis of 3,4-dihydro-2*H*-1-benzopyran (chroman) and reacts with alkenes (*e.g.* propene to yield methylchroman) or hydrogen donors (to yield *o*-cresol).[2] *o*-Hydroxybenzyl alcohol (HBA) is a well known precursor for *o*-QM through elimination of water.[3] Direct detection of *o*-QM by gas chromatography is not feasible, due to its high reactivity towards a large range of organic compounds or di- and tri-merization reactions.[4] Only IR[4c,4e,5] and UV[4a] spectroscopy have been successfully applied to samples collected at 77 K containing *o*-QM. To our knowledge, only Eck *et al.*[3] have detected *o*-QM at higher temperatures by photoelectron spectroscopy upon thermal treatment of HBA between 373 and 873 K. The mass spectrum of *o*-QM has never been reported. In the work described here, very low pressure pyrolysis (VLPP) with mass spectrometric (MS) detection is used as a tool for direct observation of *o*-QM as intermediate in the decomposition of HBA and chroman. We also studied the rate and product composition for the pyrolysis of 1,4-benzodioxin (BD), since it has been suggested that *o*-QM derivatives are prominent intermediates in the (photochemical) decomposition of analogous compounds, such as dibenzodioxins.[6]

Following our studies on the thermal stability of aryl ethers, in which we have established the variation of the carbon–oxygen bond strength,[2,7] two possible decomposition routes for BD can be envisaged: cleavage of the phenoxy–vinyl (route **a** in Scheme 1) or the phenyl–vinoxy bond (route **b**). Based on our recent work on phenyl vinyl ether,[7b] both reactions may be equally important, since the phenyl–vinoxy and the phenoxy–vinyl bonds are equally strong.

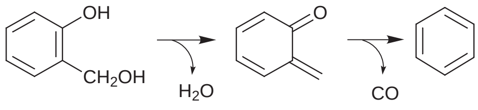


Scheme 1

Results

o-Hydroxybenzyl alcohol

Under the VLPP conditions employed, the conversion of HBA started at around 600 K and was completed above 850 K, as was found by monitoring the decay for the molecular ion ($m/z = 124$) intensity (see Fig. 1**a**). Simultaneously, the intensity for $m/z = 106$ increased, which clearly originates from *o*-quinone methide (*o*-QM). Between 850 and 900 K *o*-QM reached a maximum value and above 950 K a second product, benzene ($m/z = 78$), emerged. At more elevated temperatures the intensity for $m/z = 106$ decreased further, accompanied by an increase for $m/z = 78$. Hence, pyrolysis of HBA yields *o*-QM as intermediate, which at higher temperatures is converted into benzene [eqn. (1)], a mechanism also derived from pyrolysis studies at atmospheric pressures.[2]



(1)

Between 800 and 1000 K (at complete conversions of HBA) the 78/106 ratio remained constant (about 1 at 20 eV and 2 at 70 eV) and hence the $m/z = 78$ originates from the fragmentation of *o*-QM in the mass spectrometer. Accordingly, the recorded mass spectrum† may therefore be considered to be that for *o*-quinone methide. At higher temperatures, the change in 78/106 ratio can be used to assess the formation of benzene and this procedure has also been applied to the experimental data for chroman and BD (*vide infra*). One would expect a plateau value for *o*-QM between 800 and 1000 K since no other products were detected. However, we observed a decrease in yield which may be caused by the low MS sensitivity for *o*-QM.

Of interest are the intensities observed at $m/z = 107$ and 108

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† Intensities m/z: 109 (3), 108 (37), 107 (17), 106 (M^+, 98), 90 (3), 80 (3), 79 (9), 78 (100), 76 (2), 66 (2), 52 (7), 51 (2), 50 (16).

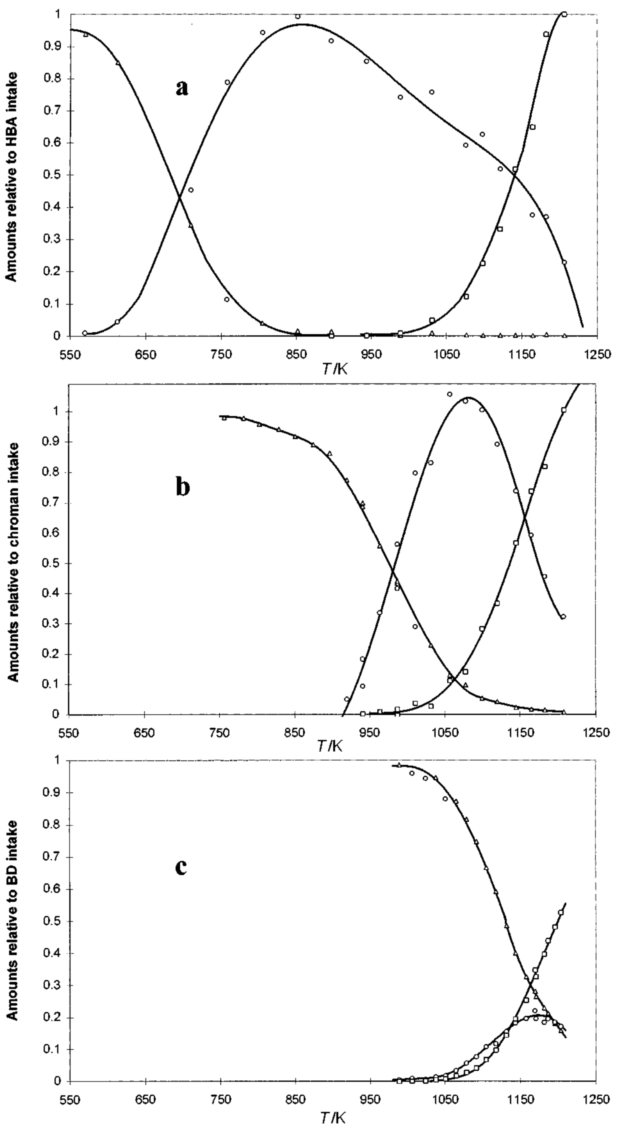
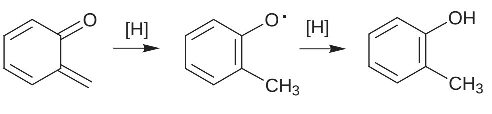


Fig. 1 Conversions of starting compound (△) and semi-quantitative yields of benzene (☐) and *o*-QM (○), in very low pressure pyrolysis experiments with *o*-hydroxybenzyl alcohol (HBA, **a**), chroman (**b**) and 1,4-benzodioxin (BD, **c**). Amounts of *o*-QM and benzene are corrected for differences in response (see text): in **a** using the response factor for benzene of 0.71 with respect to HBA; in **b** and **c** by 0.73 with respect to chroman and BD; for *o*-QM a response factor of 0.07 with respect to benzene is used in all three graphs.

which are likely to be formed from *o*-QM since the ratios $m/z = 106/107$ and $106/108$ remain constant over the entire temperature range. As was noticed before,[7b] radical species that are formed in the reaction vessel of the VLPP instrument are mainly transferred *via* (wall-associated) hydrogen transfer reactions into molecules. In the reaction pathway of HBA the elimination of water to *o*-QM is a molecular process. However, *o*-QM was found to be very reactive towards hydrogen donors[2] and may well have been transformed [see eqn. (2)] into *o*-cresol, $m/z = 108$, through similar wall mediated reactions.



(2)

o-Cresol easily loses a hydrogen atom during fragmentation; $m/z = 107/108$ is around 1 at 70 eV and 0.3 in the experimental *o*-QM spectrum. Besides $m/z = 107$ and 108, important fragments of *o*-cresol at 70 eV are $m/z = 77$ and 79. In the recorded *o*-QM spectrum at 20 eV only traces of $m/z = 77$ and 79 were observed. This means that $m/z = 107$ and 108 can be regarded as the only impurities.

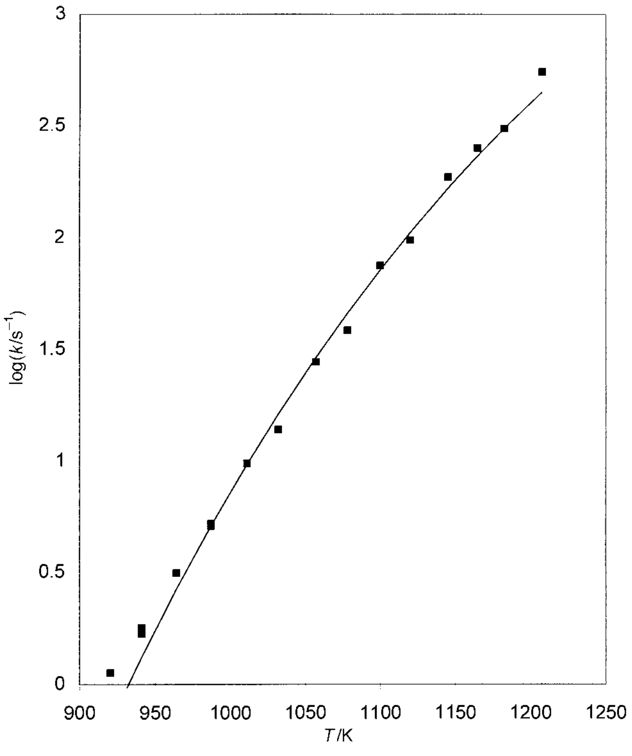
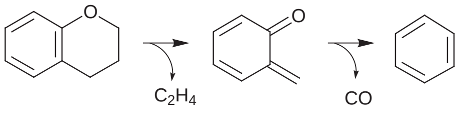


Fig. 2 Very low pressure pyrolysis data for the unimolecular decomposition of chroman (■) and RRKM calculations (solid line): $k_{\text{chroman}}/\text{s}^{-1} = 10^{15.3} \exp(-269/RT)$

Chroman

The decrease in intensity for the molecular ion peak ($m/z = 134$) as a function of the reaction temperature is presented in Fig. 2. The RRKM calculation, used to obtain the high pressure Arrhenius equation, cannot yield the preexponential factor and the activation energy simultaneously. Hence, some low frequencies of the ground state vibrational model were adjusted in such a way that log A became 15.3 (as established from measurements at atmospheric pressure).[2] The Arrhenius equation was found to obey $k_{\text{chroman}}/\text{s}^{-1} = 10^{15.3} \exp(-269/RT)$.

The change in the effluent composition (*i.e.* $m/z = 78$, 106 and 134) between 750 and 1220 K is presented in Fig. 1**b**. From the similarity of the product spectra for HBA and chroman it can be concluded that *o*-QM is an intermediate in the chroman decomposition [see eqn. (3)], as was found previously from studies at atmospheric pressures.[2] Since chroman is thermally more stable than HBA, the conversion starts at around 800 K and is almost complete at 1210 K. The conversion of *o*-QM into benzene occurs at about the same temperature compared to the thermolysis of HBA.



(3)

1,4-Benzodioxin

Preliminary thermolytic experiments at atmospheric pressure[8] for BD in nitrogen revealed that CO and benzene were the main products. The yields of carbon monoxide were always higher than those of benzene. At complete conversion of BD the CO yield approached 200% of the BD intake. However, no kinetic parameters and mechanistic conclusions could be derived from these results since the presence of the reactive vinylic bond in 1,4-benzodioxin may have caused a large fraction of radical

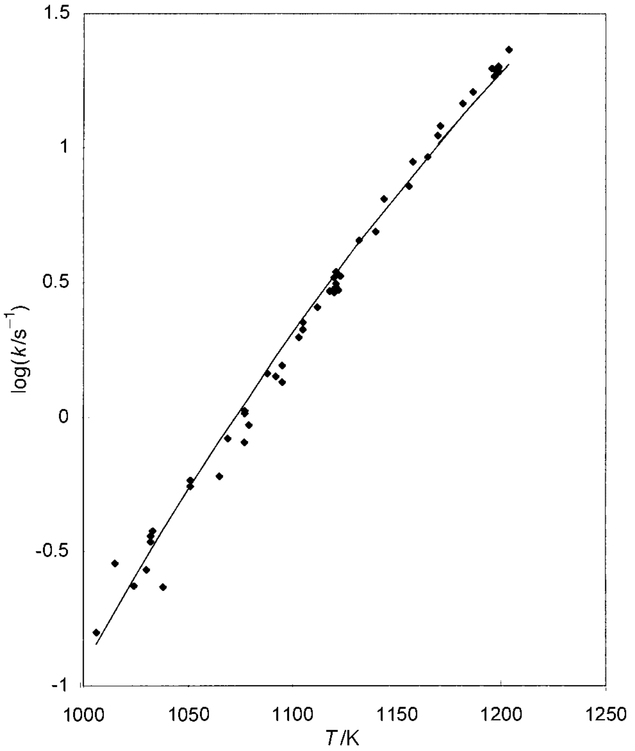


Fig. 3 Very low pressure pyrolysis data for the unimolecular decomposition of 1,4-benzodioxin (◆) and RRKM calculations (solid line): $k_{BD}/s^{-1} = 10^{15.6} \exp(-310/RT)$

induced decomposition, comparable to earlier observations with phenyl vinyl ether.[7b] The products which can be ascribed to the induced pathway were benzaldehyde, *o*-cresol, benzofuran and phenol, all at much lower yields than benzene. Besides, the carbon mass balance was quite incomplete. In the presence of a large excess of propene as bath gas for the pyrolysis, the product spectrum changed: the CO yield decreased to about 100% of the BD intake and more benzofuran and phenol were formed. However, no products derived from cyclopentadienone were found (*vide infra*).

The effluent spectrum as measured with the VLPP instrument nicely demonstrates $m/z = 78$ and $m/z = 106$ to be the major products, similar to HBA and chroman (Fig. 1**c**); no other products were evident.

The Arrhenius equation that was derived from the decrease in abundance of the molecular ion ($m/z = 134$) yielded $k_{BD}/s^{-1} = 10^{15.6} \exp(-310/RT)$. The plot, as presented in Fig. 3, was obtained after RRKM calculation using the preexponential factor of $10^{15.3}$ for bond homolysis,[7b] multiplied by 2 as the degeneracy factor for 1,4-benzodioxin. Exploring experiments with BD under shock tube conditions yielded predominantly benzene, ethyne and a number of C_4 species. Ethyne and the C_4 species are most likely formed from fulvene, one of the decomposition products of *o*-QM.[2] CO could not be measured with the apparatus used.

Quantification

The products formed during very low pressure pyrolysis cannot easily be quantified because the MS response factors are not known. From earlier experiments we found that, in general, responses of various molecules, as calculated from their molecular ion abundances at 20 eV, are in the same order of magnitude. In the current experiments response factors have been derived by comparing the intensities for the molecular ion of the product at *ca.* 100% conversion with the intensity for the molecular ion of the reagent at 0% conversion. By applying these response factors, the semi-quantitative product plots in Fig. 1 are obtained. In the pyrolysis of HBA, the relative response factor of benzene with respect to HBA is 2.27 (determined at 1210 K, based on the assumption that all HBA is converted into benzene). HBA fragments substantially, even at 20 eV, mainly to $m/z = 78$, 106 and 124 in about equal intensities. Thus, applying the sum of these intensities the response factor of benzene becomes 0.71. The response for *o*-QM, using the molecular ion intensity, is much smaller than that of the investigated compounds or benzene. From the experiment with HBA for *o*-QM ($m/z = 106$ at 850 K) with respect to benzene ($m/z = 78$ at 1210 K) and normalized for the HBA intake, a relative response factor of 0.07 is retrieved. The low value for *o*-QM is rather surprising in view of its high reactivity. In case of chroman, assuming complete conversion at 1210 K, a response factor for benzene with respect to chroman ($m/z = 134$) of 0.73 is found, a value which was also applied for the experiments with BD.

Discussion

o-Hydroxybenzyl alcohol

Decomposition of *o*-hydroxybenzyl alcohol gives exclusively *o*-quinone methide (and water) as has been demonstrated by the very low pressure pyrolysis experiments. These findings are in accordance with our earlier observation[2] that the pyrolysis of HBA at atmospheric conditions at 700 K in the presence of an alkene (propene), yields almost quantitatively methylchromane, with *o*-QM as the intermediate. However, HBA may not be a suitable precursor for *o*-QM under different reaction conditions: thermolysis in the liquid phase, as in lignin liquefaction at around 450 K. Some degree of water elimination (to *o*-QM) occurs but the ionic chemistry (intra- or inter-molecular protonation of the benzylic hydroxy group to give a carbocation) appears to be more important.[9] In the presence of an alcohol, the formation of an ether derivative is not due to the addition of ROH to *o*-QM, as has been postulated previously,[10] but can be better explained by the benzylic cation interaction with the oxygen of the alcohol.[9]

Chroman

The obtained activation energy of 269 kJ mol⁻¹ is somewhat higher (6 kJ mol⁻¹) than found in our previous investigations under atmospheric pyrolytic conditions.[2] This difference may be real, in view of the experimental uncertainties of around 4 kJ mol⁻¹ associated with both experimental approaches. In principle, two thermolytic pathways exist for chroman: a concerted (*retro* Diels–Alder) route and a biradical mechanism, both to yield ethene and *o*-quinone methide as the primary products. Based on the observed stereochemistry for the reverse reaction, *i.e.* addition of but-2-ene to the *o*-QM following a Diels–Alder mechanism and the rate parameters for the disappearance of chroman, the contribution of both routes to the overall process could not be established. In general, a clear distinction can be expected between a concerted and a biradical pathway, with the former to display a lower E_a value and a lower frequency factor, due to the more tight transition state. The VLPP experiments have been conducted at higher temperatures (50% conversion was reached at 980 K while at atmospheric pressure 50% conversion occurred at 860 K) and as a consequence, the biradical pathway may well be more prominently present, accompanied by an increase for the experimental activation energy. From the slightly higher value for E_a we may conclude that the biradical pathway is already the major pathway above 800 K.

The difference of 19 kJ mol⁻¹ between the E_a (273 kJ mol⁻¹ at 298 K)‡ as derived in this study and the calculated phenolic–carbon bond strength (254 kJ mol⁻¹)[2] can be identi-

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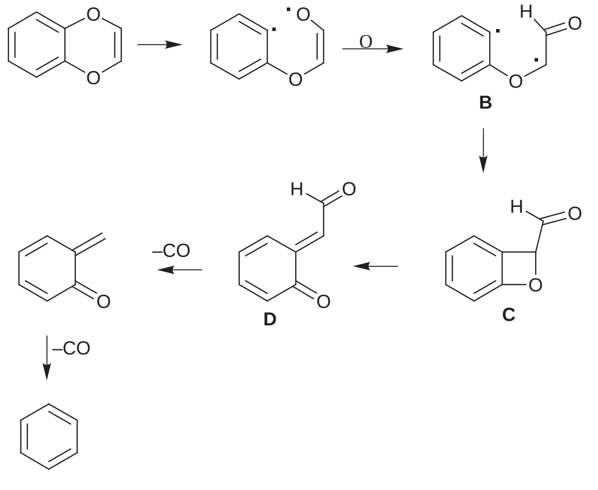
‡ Using $E_d = E_a - \Delta_r C_p(1130 - 298)$ with $\Delta_r C_p$ derived from the difference in the RRKM computed entropies for reactant and transition state at 1130 and 298 K.

fied as rotational energy, as has been reported for tetralin[11] and 2,3-dihydrobenzodioxin.[7c]

1,4-Benzodioxin

The mechanism, *i.e.* the contributions of route **a** and **b** in Scheme 1, for the thermal decomposition of BD can be derived from the observed products. In the low pressure experiments with BD the only reaction products are *o*-QM and benzene, thus it can be concluded that route **b** is the major pathway. More indirect experimental evidence supports this mechanism. Thermolytic experiments with 1,4-benzodioxin, highly diluted in nitrogen, did not reveal any substantial amount of ethyne: the elimination product from the biradical formed in route **a**, analogously to the chroman decomposition.[2] Simultaneously, the second product, benzoquinone, readily eliminates CO under these high temperature conditions. The obtained cyclopentadienone can be trapped by propene to yield methylcyclohexadienes (and eventually toluene) quantitatively.[7c] Since these products were not found in the product mixture after thermolysis in propene, it can be concluded that route **b** is the major pathway.

The product forming steps after route **b** are given in detail in Scheme 2. After cleavage of the phenyl–vinoxy bond, the free electron will be mainly located on the carbon atom (as in the vinoxyl radical) and the subsequent radical–radical coupling leads to a thermally unstable 4-ring species, **C**. Rupture of the weak phenoxy–carbon bond yields a quinone methide derivative, **D**. If **D**, an isomer of BD, is stable under the employed VLPP conditions, the intensity for $m/z = 134$ would not decrease. Moreover, it is known that in the mass spectra of aldehydes, even at low ionization potentials, the M − 1 fragment is predominantly present.§ The product spectra did not show any significant change for the 133/134 mass ratio, which implies that conversion of **D** through the elimination of CO is relatively fast. Thus, the rate of disappearance for **D** needs to be at least 100-fold faster than its formation rate to comply with these observations. According to a consecutive reaction scheme and with a frequency factor of $10^{13.5}$ s^{-1}, similar to that for the molecular CO elimination from acrolein derivatives [eqn. (4)],[12] an activation energy is calculated to be



Scheme 2

$$\mathrm{R{-}CH{=}CH{-}CHO \longrightarrow R{-}CH{=}CH_2 + CO} \qquad (4)$$

around 230 kJ mol^{-1} at 1150 K. Compared with other unsaturated aldehydes,[13] the E_a is somewhat lower (*ca.* 20 kJ mol^{-1}) and may reflect the higher hydrogen affinity of the conjugated electronic system in quinone methides.

The radical–radical recombination to the intermediate **C** can be considered as a non-activated reaction. Hence, the measured E_a is equal to the E_d of the phenyl–vinoxy bond in 1,4-benzodioxin and amounts to 310 kJ mol^{-1} at 1150 K or 313 kJ mol^{-1} at 298 K.‡ This value deviates somewhat from that for the bond dissociation energy for the phenyl–vinoxy bond ($E_d = 322$ kJ mol^{-1})¶ in phenyl vinyl ether at 298 K. A larger weakening effect would have been expected due to the presence of a second oxygen as a substituent.[7d,14] However, the comparison with phenyl vinyl ether may not be allowed because of the conformational difference between both compounds. DFT calculations have shown that in phenyl vinyl ether the vinyl group is oriented orthogonally to the aromatic ring, while BD is planar. The bond strengths for aryl ethers (Ph–O–R) are strongly influenced by the interaction between the lone pair of oxygen with the π-electrons of the aromatic ring. This interaction is optimal when the Ph–O–R bond lies in the aromatic plane such as in phenol and alkyl phenyl ethers. Forcing the R outside the plane of the ring changes (lowers) the E_d for Ph–OR and also for PhO–R. 2,3-Dihydro-1,4-benzodioxin is a better compound to compare with, although the structure is not completely flat either.|| With group additivity the phenyl–oxygen bond is calculated to be 418 kJ mol^{-1}.** The weakening by 105 kJ mol^{-1} in 1,4-benzodioxin can easily be related to the resonance stabilization energy in the vinoxyl radical (84 kJ mol^{-1}),[7b] together with an additional stabilization energy due to the oxygen substituent (21 kJ mol^{-1}) at the olefinic moiety in the corresponding biradical. The latter value is comparable with the effect by an *ortho* methoxy group on the $E_d(\mathrm{O{-}CH_3})$ in *o*-dimethoxybenzene.[7d,14]

Using the heat of formation for 1,4-benzodioxin (−101 kJ mol^{-1})†† and the E_d for the phenyl–vinoxy bond (313 kJ mol^{-1}), the heat of formation for the intermediate **B**, formed after bond cleavage, can be computed as 212 kJ mol^{-1}. The same intermediate, **B**, is also obtained after abstraction of two hydrogen atoms from PhOCH$_2$CHO. Using its heat of formation (−184 kJ mol^{-1})‡‡ and E_d(Ph–H) = 468 kJ mol^{-1},[7b] the $E_d(\mathrm{C_\beta{-}H})$ in PhOCH$_2$CHO can be estimated as 364 kJ mol^{-1}. With an $E_d(\mathrm{C_{sec}{-}H})$ for secondary carbons of 410 kJ mol^{-1} and a stabilization by carbonyl group (−25 kJ mol^{-1}),[7b] the additional stabilization by the neighboring oxygen becomes 21 kJ mol^{-1}, consonant with other thermochemical data.[13] Bordwell and Zhang[18] measured a value of 337 kJ mol^{-1} for $E_d(\mathrm{C_\beta{-}H})$ in PhOCH$_2$C(O)Ph§§ by an electrochemical cycle method in the liquid phase. Given the above considerations, it seems highly unlikely that the radical stabilization by a neighboring oxygen would be as high as 48 kJ mol^{-1}. It should be kept in mind that the kinetic parameters for 1,4-benzodioxin are retrieved from the (overall) rate of disappearance. The fact that

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§ In the VLPP experiments with phenyl vinyl ether at high concentrations,[7b] benzaldehyde was detected as a minor product. At 1210 K, the ratio $m/z = 105/106$ amounted to 0.6 at 20 eV.

¶ Using $E_d = E_a + RT_m - \Delta_rC_p(T_m - 298)$ with E_a, T_m and Δ_rC_p from ref. 7*b*.

|| 2,3-Dihydrobenzodioxin has a twisted boat conformation with a dihedral angle of around 15° for the phenoxy linkage, as calculated by AM1.

** Using group additivities, starting with ethyl phenyl ether,[15] Δ_fH_{298}-(PhOCH$_2$CH$_2$OH) = −253 kJ mol^{-1}. Applying a E_d(Ph–H) = 468 kJ mol^{-1},[7b] and a E_d(O–H) = 438 kJ mol^{-1} (from ethanol),[16] Δ_fH_{298}-[Ph(·)OCH$_2$CH$_2$O·] (= **B**) becomes 217 kJ mol^{-1}. With Δ_fH_{298}(2,3-dihydrobenzodioxin) = −201 kJ mol^{-1},[15] the E_d(Ph–O) in 2,3-dihydrobenzodioxin is 418 kJ mol^{-1}.

†† From the difference in Δ_fH_{298} of 2,3-dihydro-1,4-dioxin and 1,4-dioxin a heat of dehydrogenation is found of 100 kJ mol^{-1}.[17] With a Δ_fH_{298} for 2,3-dihydro-1,4-benzodioxin of −201 kJ mol^{-1},[15] Δ_fH_{298} for 1,4-benzodioxin becomes −101 kJ mol^{-1}.

‡‡ By group additivities, starting with ethyl phenyl ether.[15]

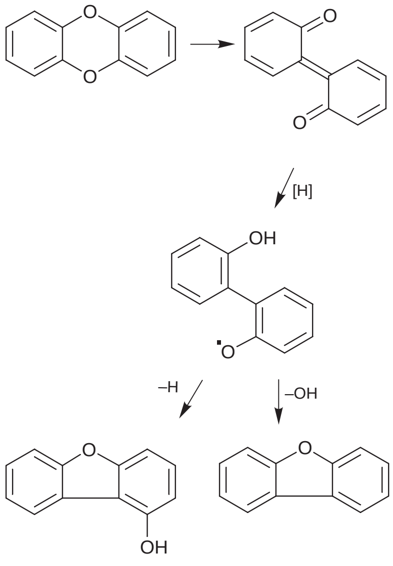
§§ PhOCH$_2$CHO and PhCH$_2$C(O)Ph can be compared since a H or Ph next to the carbonyl moiety do not influence the E_d(C–H) of the CH$_2$ group. For comparison: the E_d(C–H) in H–CH$_2$CHO and H–CH$_2$-C(O)Ph are equal within the reported error margins.[7b,16,19] only route **b** is observed does not imply that the cleavage of the phenoxy–vinyl (route **a**) does not occur at all. According to a bond strength assessment, the phenoxyl-vinyl bond is even 5 kJ mol^{-1} weaker than the phenyl–vinoxy bond.¶¶ The intramolecular radical–radical coupling after bond rupture will not increase the activation energy associated with route **b**. In contrast, for the elimination of ethyne in route **a** a rotational energy needs to be added to the initial activation energy for bond cleavage (*vide supra*).[7c,9] Moreover, the interaction of the vinylic π-system with the neighboring oxygen lone pair imposes an additional energy term for that exit channel. This phenomenon is exemplified by eqns. (5) and (6). With R = H or CH_3

$$RCH_2\text{–}CH_2^{\bullet} \longrightarrow R^{\bullet} + CH_2\text{=}CH_2 \qquad (5)$$

$$RCH\text{=}CH_2^{\bullet} \longrightarrow R^{\bullet} + CH\equiv CH \qquad (6)$$

no difference in activation energies between eqns. (5) and (6) is found, whereas when R = OH the elimination of ethyne requires 27 kJ mol^{-1} more than the elimination of ethene.[13] With these considerations, the exit barrier for the product forming step for route **a** may well require (including the rotational energy) at least 40 kJ mol^{-1}, which means that pathway **a** is completely reversible relative to pathway **b** under the applied reaction conditions.

Analogously to 1,4-benzodioxin, the decomposition of dibenzo[1,4]dioxin renders an intermediate containing the quinone methide structure. This intermediate can easily incorporate hydrogen, leading to a substituted phenoxyl radical (Scheme 3). Subsequent ring closure, *i.e.* the addition of the phenoxyl radical to the other aromatic moiety, gives rise to two products: dibenzofuran and hydroxydibenzofuran. These products were indeed found upon pyrolyzing dibenzo[1,4]dioxin in a hydrogen atmosphere at temperatures of around 1000 K.[8]



Scheme 3

Experimental

Very low pressure pyrolysis

The VLPP instrument has been described before.[7b,20] The reagents were introduced into the reaction chamber by means of sublimation (HBA at 355 K, sublimation vessel wrapped with heating tape) or vaporization (chroman and BD at 273 K, evaporation vessel in melting ice). The product mixture was sampled continuously by a mass spectrometer (Hewlett-Packard 5790) in the range of m/z = 15–140 amu. An ionization energy of 20 eV was used to reduce fragmentation of the reagent and products. After temperature equilibration, 1000–2000 scans were averaged to improve the signal : noise ratio. Intensities were corrected for amounts that arose from the fragmentation of the starting compound as recorded during blank runs at temperatures where no conversion was observed. The intake at high temperatures was calculated by interpolation of the blank runs. In the case of chroman and BD the rate constants according to unimolecular decay were calculated and by use of the RRKM algorithm[21] the Arrhenius expression for high pressure was obtained, similar to the procedure described before.[7b]

Atmospheric pressure pyrolysis

Thermolysis experiments were performed in a plug flow microreactor (5 ml) system fitted with on-line GC analysis, which has been fully described before.[7c] Typically, the BD concentrations were around 12 μmol l^{-1} in nitrogen and 7 μmol l^{-1} in propene–nitrogen mixtures (3 : 1). Residence times were around 6 s.

Shock tube experiments

The experimental set-up has been described before.[22] Experiments were performed with neat BD or with added mesitylene (1,3,5-trimethylbenzene) to scavenge free radicals. 4-Methylcyclohexene was used to monitor reaction temperatures.

Chemicals

Propene (Air Products 99.0%) was used as such; nitrogen (Air Products 99.995%) was passed through moisture and charcoal filters prior to use. HBA (Aldrich 99%) was purified through sublimation. The synthesis of chroman has been described before.[2] The synthesis of 1,4-benzodioxin was carried out following a slightly modified procedure of Farina and Zecchi.[23] Treatment of 2,3-dihydro-1,4-benzodioxin with excess *N*-bromosuccinimide, under free radical conditions,[24] gives 2,3-dibromo-1,4-benzodioxin, which is debrominated by sodium iodide. A solution of 2,3-dihydro-1,4-benzodioxin (37 mmol; Janssen Chimica 99%) in dry tetrachloromethane (150 ml) was refluxed using an infrared lamp as heat and light source. *N*-Bromosuccinimide (85 mmol) and 2,2′-azobis(isobutyronitrile) (initiator) were added over a period of about 6 h. The complete conversion was confirmed by GC. The resulting solution was filtered and the solvent removed under reduced pressure. The crude 2,3-dibromo-1,4-benzodioxin was dissolved in acetone (150 ml) and refluxed. NaI (185 mmol) was added over a period of 2.5 h. The solvent was removed under reduced pressure and the residue dissolved in a mixture of diethyl ether (150 ml) and a 0.5 M $Na_2S_2O_3$ solution (100 ml) to remove traces of bromine. The water layer was extracted twice with diethyl ether (20 ml). The diethyl ether extracts were combined, washed with water (40 ml) and dried on $MgSO_4$. Purification by silica gel column chromatography (*n*-hexane as eluent) yielded 3.6 g (71%) of BD which appeared as a yellowish oil of 99% purity. The product was analyzed by GC–MS (70 eV) and ^1H NMR (200 MHz in CCl_4, JEOL JNM FX200). m/z 134 (M^+, 100), 106 (3), 105 (24), 78 (73), 77 (38). δ_H 6.52–6.75 (m, 4H), 5.78 (s, 2H), in accordance with earlier observations.[25] From the NMR absorptions it can be established that the vinylic protons in BD and in cyclohexene appear at the same magnetic field strength, thus orbital overlap and electron delocalization in the heteroatom ring is limited. Therefore, the oxygen containing ring can be considered as anti-aromatic which has been experimentally confirmed: reaction of 1,4-benzodioxin with a solution of Br_2 in CCl_4 results in exclusive formation of the dibromo-derivative.

¶¶ From group additivity rules, starting with phenyl vinyl ether,[7b] Δ_fH_{298}(2-HOPhOCH=CH$_2$) = −159 kJ mol^{-1}. By using a E_d(C$_\beta$–H) = 456 kJ mol^{-1},[7b] and a E_d(O–H) = 346 kJ mol^{-1} [from the E_d(O–H) in phenol of 364 kJ mol^{-1},[7b] and a stabilization of the *ortho* oxygen by 18 kJ mol^{-1}],[7c] the Δ_fH_{298}[2-$^{\bullet}$OPhOCH=C(·)H] (= **A**) becomes 207 kJ mol^{-1}. Thus the phenoxy–vinyl bond strength in BD is 308 kJ mol^{-1}.

Computational procedures

Density functional theory (DFT)[26] calculations were performed using the GAUSSIAN94-D4 package[27] on an IBM RISK/6000 workstation. For the geometry optimization and frequency calculations for chroman and BD, the B3LYP functionals were employed on the 6-31G(d) basis set. A factor of 0.97 for the calculated vibrational frequencies was used to correct for the anharmonicity of the molecular vibrations.[28]

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