Thermal Decomposition of Chroman. Reactivity of *o*-Quinone Methide

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The gas phase thermal decomposition of 3,4-dihydro-2*H*-1-benzopyran (chroman, **1**) has been studied between 760 and 1110 K in different bath gases and hydrogen donors. In nitrogen, the unimolecular rate parameters are k_1 (s^{-1}) = $10^{15.3}$ exp(−263 (kJ mol^{-1})/RT). The activation energy is slightly higher than the bond dissociation energy (BDE) of the phenoxylic C−O bond. The decomposition starts with elimination of ethene and formation of 6-methylene-2,4-cyclohexadien-1-one (*o*-quinone methide, **2**). Quinone methides are important intermediates in the chemistry of lignin. In the high temperature range (860−980 K) **2** decomposes cleanly into CO, benzene, and small amounts of fulvene, obeying k_2 (s^{-1}) = $10^{14.8}$ exp(−281 (kJ mol^{-1})/RT). Reverse radical disproportionation of **2** with toluene is mainly responsible for *o*-cresol formation. In *cis*-2-butene at 770 K, exclusively *cis*-2,3-dimethylchroman is formed. This stereospecificity suggests a concerted retro-Diels−Alder mechanism and is not compatible with the high Arrhenius parameters, indicative of a stepwise, biradical mechanism.

Introduction

A large variety of aryl ethers is present in natural composite materials such as lignin. For a long time, the thermal properties of lignin have been a challenge for chemists in order to derive useful feed stock molecules from this renewable source. In the recent years we have studied the thermal behavior of acyclic and cyclic aryl ethers like methoxybenzene,[1] diphenyl ether,[2] phenyl vinyl ether,[2] 2,3-dihydro-1,4-benzodioxin,[3] and 1,4-benzodioxin.[4] Under well controlled conditions the structural influence on the energetics of the phenoxylic C−O bond could be established. In case of 2,3-dihydro-1,4-benzodioxin a biradical mechanism has been suggested as the first step in the thermal degradation, to yield *o*-benzoquinone as an intermediate. Recently, the thermal behavior of another lignin model compound, *o*-methoxyphenol, and derivatives has been studied under radical chain conditions.[5] The occurrence of *o*-cresol in the pyrolysate suggested that 6-methylene-2,4-cyclohexadien-1-one (*o*-quinone methide, **2**) may be a key intermediate. Despite the fact that quinone methides are known to be important intermediates in the conversion of lignin,[6] only a few studies (mostly at one temperature) are dealing with the chemistry of **2**. In the presence of alkenes, products stemming from cycloaddition (Diels−Alder type) are reported.[7]

The reactivity of **2** in the gas phase in a hydrogen atmosphere has been demonstrated, and addition of a hydrogen atom was suggested as the first step in the formation of *o*-cresol.[7a] At high temperatures, **2** eliminates CO, leading to formation of benzene and fulvene.[8] Turner, in his review,[9] has discussed the susceptibility in the liquid phase of the terminal methylene group toward nucleophilic attack.

Different precursors are available for the thermal or photochemical generation of **2**, depending on the temperature region and phase of interest, such as *o*-(methoxymethyl)phenol,[10] *o*-hydroxybenzyl alcohol,[11] *o*-[(methylthio)methyl]phenol,[12] and benzofuran-2(3*H*)-one.[7e,8,13] By analogy with 2,3-dihydro-1,4-benzodioxin,[3] 3,4-dihydro-2*H*-1-benzopyran[7a] (chroman, **1**) is also a precursor for **2**. Since accurately determined kinetic parameters for the decomposition of **1**, indicative for the followed route, are not available, we investigated the thermal behavior of **1** under various reaction conditions. For formation of **2** at lower temperatures *o*-hydroxybenzyl alcohol (**3**) was used. In this report a complete profile for the thermolysis of **1** over a wide temperature range (760−1110), as well as for the reactivity of **2**, is presented in order to obtain mechanistic and kinetic information.

Results

Thermal Decomposition of 1 and 3: Products. Thermolysis between 774 and 903 K of **1** (initial concentration: ca. 3 × 10^{-6} M) dissolved in excess toluene (to serve as a radical scavenging agent) in a nitrogen gas stream yielded ethene and *o*-cresol as the main products

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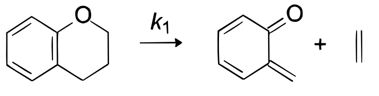
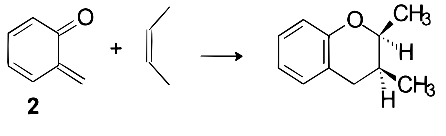
stemming from **1**; *o*-quinone methide (**2**) could not be detected. Other compounds such as benzene and styrene originated from the toluene carrier, as was demonstrated by switching from toluene to xylene. The yield of ethene corresponded well with the amount of converted chroman. The yield of *o*-cresol increased from 0 to 18% with respect to ethene. However, the carbon mass balance remained far below 100%. To explore the fate of **2**, thermolysis experiments were performed using hydrogen instead of nitrogen as the carrier gas. In this case the yield of *o*-cresol increased to 83% (903 K), while the degree of conversion of **1** (ca. 90%) did not change. With propene as the bath gas, at 883 K, both isomers 2- and 3-methylchroman emerged with a total yield of about 40% on converted **1** (ethene could not be quantified since it was already present as an impurity in the propene). One isomer, 2-methylchroman,[14] was formed in more than sixfold excess to the other. Other products were *o*-cresol (4%) and benzofuran (12%). To verify if **2** was still present in the exit stream from an experiment with **1**, toluene, and nitrogen, we added propene directly after the reactor. No methylchromans were detected, and the product composition remained unchanged.

These observations suggest that the first step in the thermolysis of **1** is the elimination of ethene and the formation of *o*-quinone methide (**2**) (eq 1). Subsequently, **2**, which appears to be thermally stable in this temperature region, reacts (partially) with hydrogen, propene or toluene.



1 **2** (1)

To study the reactivity of **2** at a lower temperature range (674−883 K), 2-hydroxybenzyl alcohol (**3**), dissolved in toluene, was used as precursor. The conversion of **3** into **2**, under elimination of water,[11a] was quantitative under our reaction conditions. In propene a large amount of **2** was converted into both methylchromans, the amount decreasing with temperature (80% at 704 K, 1% at 883 K, based on intake of **3**). Over this temperature range, the ratio 2-methylchroman:3-methylchroman changed from 19:1 to 6:1, indicating that the isomer ratio becomes thermodynamically controlled. Experiments with **3** in a mixture of nitrogen/*cis*-2-butene at a ratio of 4/6 showed a complete conversion above 766 K into only one major product ($m/z = 162$). On the basis of ^{1}H-NMR analysis (see Experimental Section) it could be concluded that this was exclusively *cis*-2,3-dimethylchroman (eq 2).



2 (2)

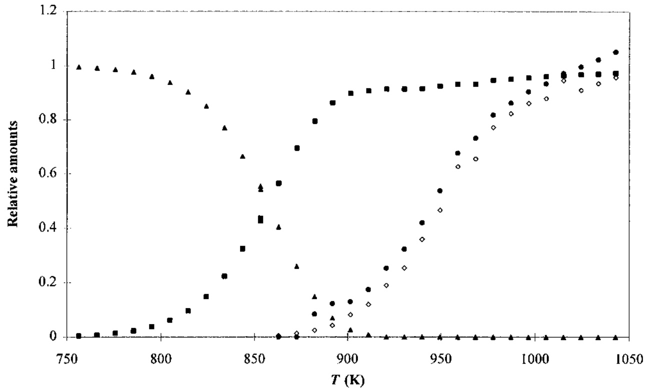


Figure 1. Product composition for the thermolysis of chroman (▲): ethene (■), CO (●), and benzene + fulvene + 1-buten-3-yne (◇).

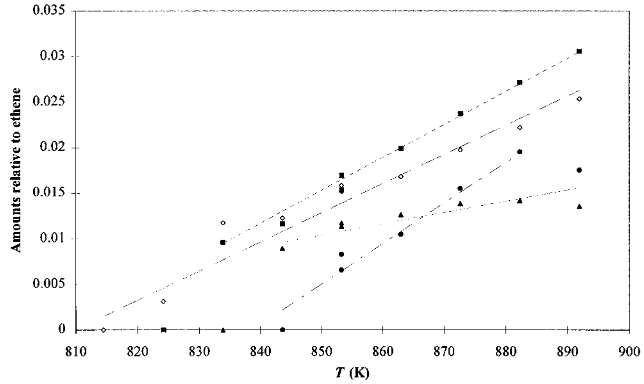


Figure 2. Relative (to ethene) amounts of *o*-cresol (■), benzofuran (◇), 2-methyl-2,3-dihydrobenzofuran (▲), and dimer (●) during the thermolysis of chroman.

Only small amounts of *o*-cresol were formed in hydrogen (4% at 674 K, 7% at 704 K, no other products could be detected) or in methane (0% at 673 K, 6% at 730 K). Traces of *o*-ethylphenol were found as a possible product from addition of methane to **2**.

Thermolysis of 1 and 2: Kinetics. Thermolysis of **1**, highly diluted (10^{-6} M) in nitrogen, over a wide range of randomly varied temperatures was performed. The product profile between 750 K and 875 K almost exclusively consisted of ethene (see Figure 1).

Minor products in the thermolysis of **1** were *o*-cresol, benzofuran, and 2-methyl-2,3-dihydrobenzofuran. *o*-Cresol could be quantified above 830 K (26% conversion of **1**) and reached a maximum of 1.7% on the intake of **1**, at 873 K (76% conversion, the highest temperature used for determination of the Arrhenius parameters). Over the same temperature range benzofuran was detected up to 1.4% and 2-methyl-2,3-dihydrobenzofuran to around 1%. Traces (<0.5%) of 2,3-dihydrobenzofuran, 2-methylbenzofuran, and *o*-allylphenol (identified by retention time and/or GC-MS) were found. Starting at 855 K, a high boiling product (**A**) was observed (1.5% at 873 K). The identity could not be established by GC-MS, but based on retention time a dimerization product of **2** is the most likely candidate. The ratio of *o*-cresol/ethene, benzofuran/ethene, and **A**/ethene increased almost linearly with temperature, but the ratio 2-methyl-2,3-dihydrobenzofuran/ethene remained almost constant (see Figure 2).

First-order behavior was verified by stepwise changing the concentration of **1** at 853 K. After an increase in concentration of in total a factor of 1.85 the same conversion (46%) was maintained. At the same time, the ratios of *o*-cresol, benzofuran, **A**, and 2-methyl-2,3-

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[14] GC-MS showed two compounds (methylchromans) with identical spectra. According to a Diels−Alder pathway the regiospecificity (frontier orbital theory) would predict that formation of 2-methylchroman is favored.[15] When a biradical route is followed the most stable intermediate arises when the bond is formed between the CH_2 in **2** and the primary CH_2 in propene. This also leads to 2-methylchroman.

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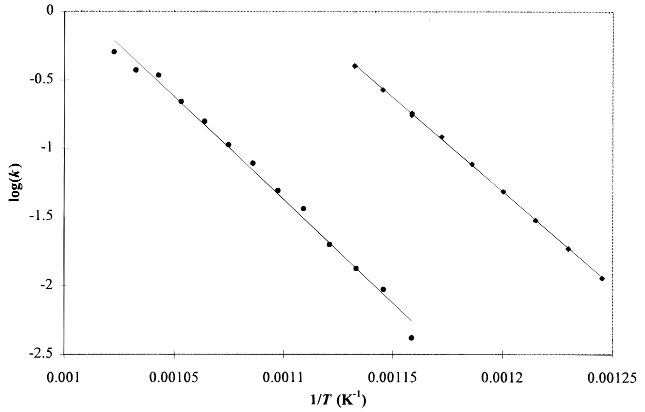


Figure 3. Arrhenius plots for unimolecular decomposition of chroman (◆) k_1 (s^{-1}) = $10^{15.3}$ exp(−263 (kJ mol^{-1})/RT) and *o*-quinone methide (●) k_2 (s^{-1}) = $10^{14.8}$ exp(−281 (kJ mol^{-1})/RT).

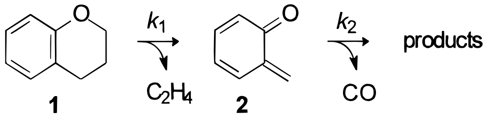
dihydrobenzofuran over ethene increased by factors of 1.6, 1.6, 7, and 1.3, respectively. With the measured product composition the unimolecular rate constants, k_1, were derived, assuming plug flow behavior, according to:

$$k_1\tau = -\ln\left(\frac{[\text{chroman}]_t}{[\text{chroman}]_{t=0}}\right) \tag{3}$$

where τ is the residence time, $[\text{chroman}]_t$ the final, and $[\text{chroman}]_{t=0}$ the initial concentration of **1**. The latter was taken equal to the sum of remaining chroman, ethene, and 2-methyl-2,3-dihydrobenzofuran, in agreement with control measurements at 523 K. The Arrhenius expression was obtained from linear regression (Figure 3) of log(k_1) *vs* T^{-1} and found to obey k_1 (s^{-1}) = $10^{15.3 \pm 0.2}$ exp(−263 ± 2 (kJ mol^{-1})/RT).

At higher temperatures (around 870 K) the thermal degradation of **2** started and carbon monoxide appeared as the prominent product, together with benzene (Figure 1) and small amounts of fulvene (based on retention time and GC-MS).[16] The ratio fulvene/benzene remained at about 10/90 between 900 and 950 K, decreasing to 2/98 at 1006 K and, finally, fulvene disappeared (T > 1040 K). At temperatures above 930 K smaller quantaties (≤2%) of ethyne and a C4-species (based on retention time), most likely 1-buten-3-yne, were found. The ratio ethyne/1-buten-3-yne was close to unity and remained constant with the temperature. Both compounds are likely to emerge from the decomposition of fulvene. Conversion of ethene into ethyne is highly unlikely under these conditions.[17] At about 1000 K the product mixture consisted of almost equimolar amounts of CO, benzene, and ethene. At higher temperatures the yield of CO is clearly more than the initial amount of oxygen in the feed (see Figure 1). Even after removal of **1** from the evaporation vessel and flushing the system with nitrogen, CO as the only compound could still be detected for hours when the reactor temperature was set at 1150 K. The initial yield amounted to about 15% of the original intake of **1** in the thermolysis experiments. Clearly, at these high temperatures gasification of accumulated oxygen containing oligomers of **2** is responsible for the CO production.

The correlation between both rate constants (eq 4) for decomposition of **1** and **2** (k_1 and k_2, respectively) can be derived according to a consecutive kinetic scheme (eq 5),[18] in which a possible dimerization of **2** is ignored in view of the high reaction temperatures and low concentrations of **2**.



1 **2** (4)

$$[\text{products}]_t = [\text{chroman}]_{t=0} \times \left\{1 - \frac{k_1k_2}{k_2 - k_1}\left(\frac{\exp(-k_1\tau)}{k_1} - \frac{\exp(-k_2\tau)}{k_2}\right)\right\} \tag{5}$$

In this expression $[\text{chroman}]_{t=0}$ is the initial concentration of **1** (taken equal to the sum of ethene, 2-methyl-2,3-dihydrobenzofuran, and remaining chroman) and $[\text{products}]_t$ the final concentration of products, *i.e.* the sum of the measured concentrations of benzene, fulvene, and 1-buten-3-yne. Based on these calculated values for k_2, an Arrhenius plot (Figure 3) yielded the rate expression: k_2 (s^{-1}) = $10^{14.8 \pm 0.3}$ exp(−281 ± 6 (kJ mol^{-1})/RT). This rate of decomposition of **2** is lower than the comparable CO elimination from *o*-benzoquinone.[3] In that case the decomposition was complete at these temperatures. Both the thermolysis of **1** and **2** have been repeated and found to be reproducible.

Discussion

The main process in the thermolysis of chroman (**1**) is cleavage into ethene and *o*-quinone methide (**2**). The kinetics will be discussed in next section, followed by an elaboration on the reactivity of **2** under different conditions, to include its thermal decomposition.

Thermolysis of 1: Kinetics. Two possible routes can be envisaged for decomposition of chroman: a biradical pathway similar to that reported for 2,3-dihydro-1,4-benzodioxin[3] and 1,2,3,4-tetrahydronaphthalene,[19] and a concerted, retro-Diels−Alder mechanism.[20] In general, the observed kinetic parameters are indicative for the preferred pathway. A biradical pathway has been concluded for 2,3-dihydro-1,4-benzodioxin and 1,2,3,4-tetrahydronaphthalene because the measured activation energy (E_a) was higher than the enthalpy required to cleave the C−O/C−C bond. The differences (22 and 30 kJ mol^{-1}) between the computed bond dissociation energy (BDE) and the E_a (as derived from product measurements) were explained in terms of an additional barrier for rotation around the phenolic O−C or the benzylic C−C bond, before elimination of ethene.[3,19] The experimental energy of activation (263 kJ mol^{-1}) for decomposition of **1** is slightly above the strength of the phenoxylic O−C bond, 254 kJ mol^{-1}.[21] This suggests that only a small additional rotational energy of 9 kJ mol^{-1} needs to be incorporated. Together with the high preexponential factor, almost equal to that for 2,3-dihydro-1,4-benzodioxin, it can be concluded that the thermal de-

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[16] Fulvene was generated in a separate experiment by recombination of cyclopentadienyl radicals with chloromethyl radicals and subsequent elimination of HCl.

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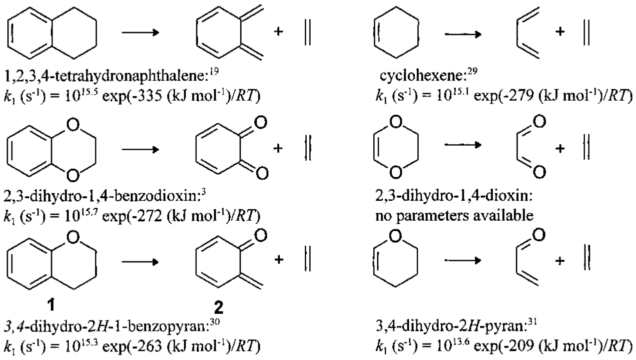
Scheme 1. Rate Parameters for the Thermolysis of 1,2,3,4-Tetrahydronaphthalene, 2,3-Dihydro-1,4-benzodioxin, 3,4-Dihydro-2*H*-1-benzopyran, Cyclohexene, 2,3-Dihydro-1,4-dioxin, and 3,4-Dihydro-2*H*-pyran



composition of **1** follows a biradical pathway. On the other hand, under the same conditions the reverse reaction, **2** with *cis*-2-butene, yielded only *cis*-2,2-dimethylchroman (eq 2), which leaves no doubt that an addition according to a concerted Diels–Alder mechanism is operative. Thus, based on the principle of microscopic reversibility, these results are contradictive.

Our results are consistent with the findings of Paul and Gajewski.[7a] In pyrolysis experiments of **1** in excess *cis*-2-butene or *trans*-2-butene they observed addition to **2** with high stereoselectivity. However, it has to be noticed that these results were obtained after thermolysis for 4.5 h at 686 K. With their reported conversions of **1**, an average rate constant can be calculated of around 8 $\times 10^{-6}$ s^{-1}, which is in reasonable accordance with our kinetic study, yielding $k_1 = 3.2 \times 10^{-6}$ s^{-1} under those conditions.

The decomposition rate parameters of **1** and structurally related compounds are compiled in Scheme 1.

The decomposition of compounds without the aromatic ring, like cyclohexene and 3,4-dihydro-2*H*-pyran, has been reported to follow a retro-Diels–Alder mechanism based on energy considerations (E_a lower than BDE of interest, see Table 1) and the stereospecificity of the reverse reactions. From Scheme 1 and Table 1 a clear difference can be noticed in behavior between the benzocyclic and cyclic compounds. This may be due to the rigidity of the aromatic ring which prevents the formation of an intermediate state necessary for the concerted decomposition.

The current study shows that the magnitude of the activation energy as such cannot be used as conclusive evidence as to the followed mechanism. For a concerted, retro-Diels–Alder process, only a small entropy change may be expected, while a biradical pathway involves a substantial increase in freedom of movement of the nonbenzoic ring. From Scheme 1, an average pre-exponential factor for decomposition of **1** and analogous compounds leads to an entropy of activation, $\Delta S^{\ddagger}$, of 34 J mol^{-1} K^{-1}, still in the wide range reported for other retro-Diels–Alder reactions (−21 to +46 J mol^{-1} K^{-1}).[35] Note that for regular bond homolysis $\Delta S^{\ddagger}$ is mostly around 35–45 J mol^{-1} K^{-1}.[17] Hence, also no conclusions can be drawn based on entropy considerations. In any case, the stereospecificity of the reverse reaction should always be taken into account. It is remarkable that this has not been done in case of 1,2,3,4-tetrahydronaphthalene,[19] where 5,6-bis(methylene)-1,3-cyclohexadiene (*o*-quinodimethane) is the initial product of decomposition. The reactivity of *o*-quinodimethane toward a dienophilic compound has been investigated extensively. In almost all cases the conclusion can be drawn, based on product stereospecificity, that the Diels–Alder addition is the preferred pathway.[36] Efforts to disentangle the course of reaction for 1,2,3,4-tetrahydronaphthalene, using a different precursor for the biradical intermediate, were inconclusive.[37]

Evidence in favor of a biradical pathway for thermolysis of 1,2,3,4-tetrahydronaphthalene[19] and 2,3-dihydro-1,4-benzodioxin[3] can be obtained from the product composition. In both cases compounds were present with retention of the CH_2CH_2 moiety: *o*-allyltoluene and 2-methyl-1,3-benzodioxole. The latter arises through bond rupture, followed by an exothermic 1,2-hydrogen shift, and subsequent ring closure. According to a similar mechanism 2-methyl-2,3-dihydrobenzofuran is expected in the thermolysis of **1** and indeed found, albeit at low yields (maximum 1.3%). This substantiates that a biradical pathway (eq 6) is present, at least to some degree.

In the last decades the transition state and mechanism of the (retro-)Diels–Alder reaction have been subject to extended experimental and theoretical studies and dis-

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[21] BDE(C–O) in **1** can be calculated using BDE(C–O) in ethyl phenyl ether (265 kJ mol^{-1})[22] and substracting 11 kJ mol^{-1}, due to the *ortho* CH_2CH_2 substituent,[23] resulting in BDE(C–O) = 254 kJ mol^{-1} in **1**. As an alternative Δ_fH(*o*-propylphenol) can be estimated to −171 kJ mol^{-1}, applying the increment (−75 kJ mol^{-1}) for replacement of hydrogen by propyl in benzene.[24] The O–H bond strength in substituted phenols can be estimated using[25] ΔBDE(O–H) = $30.63\{\Sigma(\sigma_o^+ + \sigma_m^+ + \sigma_p^+)\} - 2.68$ kJ mol^{-1}; and $\sigma_o^+ = 0.66\ \sigma_p^+$.[26] With σ_p^+(propyl) = −0.29,[27] BDE(O–H) becomes 356 kJ mol^{-1}. BDE(C–H) is taken equal to that in ethane: 423 kJ mol^{-1}.[24] Thus $\Delta_fH(C_6H_4(O^\bullet)\text{-}C_3H_6^\bullet)$ becomes 172 kJ mol^{-1} and with Δ_fH(**1**) = 82.4 kJ mol^{-1} (see Table 1), BDE(C–O) in **1** 254 kJ mol^{-1}. It should be noted that the error associated with these type of BDE calculations is in the order of 7 kJ mol^{-1}. Since both approaches resulted in the same value it can be concluded that an additional ring strain component is negligible, in accordance with ref 28.

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[34] Δ_fH(**2**) can be estimated according to increment rules: The replacement of a CH_2 by a C=O in cyclohexane to cyclohexanone or in 2,4-cyclohexadienone to give *o*-benzoquinone changes Δ_fH by −103 and −105 kJ mol^{-1}, respectively.[24] Δ_fH(**2**) can be estimated to 68 kJ mol^{-1} by applying this increment to 5-methylene-1,3-cyclohexadiene. Second approach: A change of 67 kJ mol^{-1} can be derived for the replacement of a CH_2 by a $C{=}CH_2$ in 1,3-cyclohexadiene to give 5-methylene-1,3-cyclohexadiene.[24] Applying that replacement to 2,4-cyclohexadienone yields Δ_fH(**2**) = 67 kJ mol^{-1}. AM1 calculations yielded a value of 64.5 kJ mol^{-1}. We use Δ_fH(**2**) = 66 kJ mol^{-1}.

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[36] (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873–2889. (b) Sato, H.; Isono, N.; Okamura, K.; Date, T.; Mori, M. *Tetrahedron Lett.* **1994**, *35*, 2035–2038. (c) Fleming, I.; Gianni, F. L.; Mah, T. *Tetrahedron Lett.* **1976**, 881–884.

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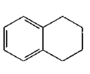
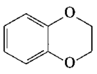
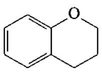
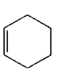
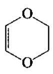
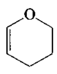
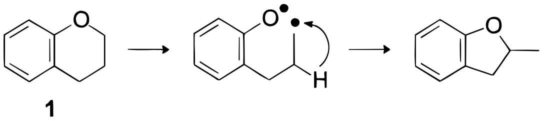
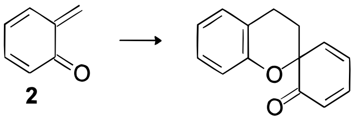
Table 1. Enthalpies, Bond Dissociation Energies and Activation Energies for Conversion of Chroman and Related Compounds under Elimination of Ethene (in kJ mol^{-1})

						
$\Delta_f H^a$	25.1	-200.8	-82.4^b	-4.6	-240.1^c	-125.1
$\Delta_f H$ (prod)^{a,d}	239^e	-104.6	66^f	110.0	-211.7	-75.3
$\Delta_r H^g$	266.2	148.5	200.7	166.9	70.7	102.1
BDE^h	305^i	252^j	255^k	313^l	253^m	256^n
E_a ^{o}	335^i	271^j	263^p	280^q		209^r

[a] Ref. 24. [b] Ref. 32. [c] Ref.33 [d] Heat of formation of the product formed after ethene elimination. [e] Calculated by replacement of a CH_2 by a $C=CH_2$ in 5-methylene-1,3-cyclohexadiene;[34] AM1 calculations yield 254 kJ mol^{-1}. [f] Ref. 34. [g] $\Delta_f H$(prod) + $\Delta_f H$(ethene)[24] - $\Delta_f H$(reactant). [h] BDE (at 300 K) of the weakest bond i.e. benzylic (1st compound), allylic (4th), phenolic (2nd, 3rd), vinoxylic (5th, 6th). [i] Ref. 19. [j] Ref. 3. [k] Ref. 21. [l] Taking in account $\Delta_f H$(*cis*-2-hexene) = -48 kJ mol^{-1},[24] BDE(C-H) in ethane (423 kJ mol^{-1})[24] and in propene (369 kJ mol^{-1})[2]: $\Delta_f H(\bullet CH_2CH_2{=}CHCH_2CH_2CH_2\bullet)$ = 308 kJ mol^{-1}. [m] BDE(2,3-dihydro-1,4-dioxin) = BDE(2,3-dihydro-1,4-benzodioxin) + BDE(2,3-dihydro-γ-pyran) - BDE(**1**). [n] Using the increase in $\Delta_f H$ from 1-propanol to 1-propene-1-ol, $\Delta_f H$(1-pentene-1-ol) = -209.2 kJ mol^{-1}.[24] Applying BDE(O-H) in ethenol (352.7 kJ mol^{-1})[2] and BDE(C-H) in ethane (423 kJ mol^{-1})[24]: $\Delta_f H(\bullet OCH{=}CHCH_2CH_2CH_2\bullet)$ = 130.5 kJ mol^{-1} . [o] To compare E_a and BDE adjustment to the actual reaction temperature by means of ΔC_p is required. In general this leads to a slightly lower BDE (4-8 kJ mol^{-1})[2]. [p] This work. [q] Ref. 29. [r] Ref. 31.



1 (6)



2 (7)

cussions.[20] The reasoning described above is based on the linkage between stereospecifity and a concerted mechanism. However, even in case of a stepwise (biradical) mechanism the stereochemical retention can be the same as for a concerted process if the second bond breaks within the time necessary for C2–C3 rotation. Very recently, Horn et al.[38] demonstrated the existence of such a process by studying the retro-Diels–Alder reactions of norbornene and norbornadiene on femtosecond timescale. In our case, the difference between the BDE and the experimental E_a (of 9 kJ mol^{-1}) has been explained as an additional barrier for rotation around the benzylic C–C axis, prior to ethene elimination. At 850 K, the rotational time around this bond will be about 0.4 ps,[38] which is most probably higher than that for the (free) rotation around the C2–C3 axis in **1**. Hence, a loss of stereospecificity is expected. Therefore, only when the E_a equals the BDE the above mechanism would explain our observations. However, the predicted BDE by enthalpy assessment will be too high rather than too low, since minor corrections (e.g. ΔC_p, see Table 1 footnote o) are not incorporated. Hence, further (computational) research will be necessary before reaching a final conclusion as to this issue.

Reactivity of 2. At temperatures as low as 273 K, several authors reported the formation of the dimer,[10a,11c,39] trimer,[10,11b,c,39] and even tetramer[39] of **2**. These oligomers are products of the Diels–Alder reaction between two molecules of **2** (e.g. eq 7).

Even under our dilute conditions and higher temperatures, the low mass balances point to formation of oligomers. These may stick to the wall of the reactor[7a] and are thermolyzed at elevated temperatures ($T > 1000$ K) to result in the formation of CO. In the presence of other reagents this oligomerization competes with other processes.

A product which arises in variable amounts is *o*-cresol, of which the presence is not affected by the followed experimental procedures. Thus far, only speculative mechanisms have been proposed.[7a] In the absence of hydrogen or a hydrogen donating reagent (toluene) small amounts of *o*-cresol were formed. As a function of temperature, the formation of *o*-cresol and benzofuran showed the same behavior (Figure 2), and therefore these compounds are likely to be formed from the same precursor. At higher initial concentrations of **1** and at a constant degree of conversion, the increase in yield of these compounds is more than proportional, suggesting that both products originate from a reaction between two quinone methides. However, it appears to be difficult to propose the ruling mechanism on thermochemical kinetic grounds. A suggestion is that first (reversible) dimerization of **2** takes place and, thereafter, thermal rearrangement of the dimer partially leads to formation of *o*-cresol and benzofuran.

In the same temperature region and in a large excess of toluene, the yield of *o*-cresol is much higher (18% at 903 K). An explanation for this result is that reverse radical disproportionation (RRD) of **2** with the hydrogen donor (toluene) takes place (eq 8).

It should be emphasized that **2** is extremely sensitive to hydrogen transfer reactions (RRD) due to the strong

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(38) Horn, B. A.; Herek, J. L.; Zewail, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 8755–8756.

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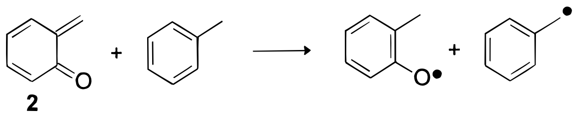


(8)

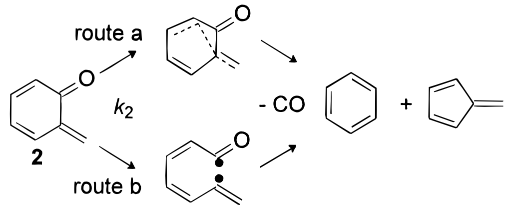
C$-$H bond that will be formed.[40] By treating the conversion of **1** into **2** and subsequently of **2** into *o*-cresol by RRD with toluene the same way as eq 5, a $k_{\mathrm{RRD,exp}}$ is derived of 12 M^{-1} s^{-1}.[42] In reality the concentration of **2** is lower due to the reversible dimerization. This would result in a higher k_{RRD} in accordance with the predicted value based on energy considerations.[42] A second route toward *o*-cresol starts with the addition of a hydrogen atom, present in the gas mixture, to **2**. The hydrogen atom concentration (5.6×10^{-14} M) can be calculated independently from the amount of methane formed by demethylation of toluene.[44] With a toluene concentration of 3×10^{-3} M and assuming a k_{add} of 10^{10} M^{-1} s^{-1},[17] $k_{\mathrm{RRD,\,exp}} \times [\text{toluene}] = 3 \times 10^{-2}$ s^{-1} is higher than $k_{\mathrm{add}} \times [H^\bullet] = 6 \times 10^{-4}$ s^{-1} and therefore RRD with toluene is faster. When the bath gas is changed from nitrogen to hydrogen the methane and hence hydrogen atom concentration increases by a factor 14. Since the rate of the RRD remains constant the increase in *o*-cresol by a factor 4 (from 0.5×10^{-6} M to 2×10^{-6} M) can be ascribed to the higher contribution of the hydrogen atom pathway. Both the RRD rate constant and the hydrogen atom concentration are temperature dependent. Therefore, both processes to yield *o*-cresol will diminish in importance with decreasing temperatures, in agreement with our observations. RRD with H_2 would be another possibility to form *o*-cresol but is too slow compared with addition of hydrogen atoms.

In a large excess of propene, at 883 K, a competition takes place between addition of propene to **2** and hydrogen transfer. Product analysis reveals a high selectivity toward addition. The rates of RRD[42] for toluene and propene are quite similar since the benzylic and allylic C$-$H BDEs are identical.[41] Under these conditions the rate constant for Diels$-$Alder addition of propene to **2**, k_{DA}[45] is around 200 times higher than k_{RRD}.

Our analyses show that, besides addition of alkenes, RRD can be an effective route for scavenging and quantifying **2**. Indeed, preliminary experiments with **3** in a pressurized liquid system in the presence of hydrogen donors (9,10-dihydroanthracene (AnH_2) and 7*H*-benz(*de*)anthracene (BenzH)) resulted in a selectivity toward *o*-cresol of 88%[46] (554 K, 1 h, **3**:BenzH:AnH_2 = 1:4:40).

Degradation of 2: Product Composition. Conversion of *o*-quinone methide yields predominantly CO and benzene, together with some fulvene. Whether fulvene and benzene are formed in a parallel or consecutive process can be judged from reported Arrhenius parameters for the exothermic (-141 kJ mol^{-1})[24] isomerization of fulvene into benzene. With a rate constant k (s^{-1}) = $10^{13,14}$ $\exp(-(268-285)\ (\mathrm{kJ\ mol^{-1}})/RT)$[47] the rate is too low to explain the change in the ratio of these compounds and hence fulvene and benzene arise from two parallel pathways, in accordance with a study by Wentrup and Müller.[8a]

Degradation of 2: Kinetics. Two possibilities can be given for the decomposition of *o*-quinone methide (**2**): Firstly, a pathway starting with cleavage of the C(=O)$-$C(=CH_2) bond, to give a biradical, followed by elimination of CO to form benzene and fulvene (eq 9, route a). Secondly, a concerted process can be envisaged (eq 9, route b).



(9)

Direct CO elimination has also been observed in the thermolysis of 3-cyclopentenone,[48] 3,5-cycloheptadienone,[48a] and 2,2,4,4-tetramethylcyclobutanone.[49] In all cases, CO elimination proceeds *via* a concerted pathway. In case of 3-cyclopentenone and 3,5-cycloheptadienone the products are acyclic, with preexponential factors of 3.3×10^{14} s^{-1} and 1.6×10^{16} s^{-1}, respectively. A better comparison can be made with 2,2,4,4-tetramethylcyclobutanone where the product of CO elimination is cyclic. The preexponential factor is reported as 8×10^{14} s^{-1}, which almost equals the value we found, namely 6.3×10^{14} s^{-1}.

The BDE for bond homolysis can be estimated to 293 kJ mol^{-1}.[50] Because the observed energy of activation, 281 kJ mol^{-1} is lower, it may be concluded that the decomposition follows a concerted mechanism. This pathway (eq 9) suggests that fulvene is the major product. However, since mainly benzene is observed and the isomerization of (ground state) fulvene is too slow, it may be that collisional not stabilized fulvene isomerizes more easily into benzene.

Conclusions

On the basis of the activation energy, the thermolysis of **1** starts with the cleavage of the phenolic C$-$O bond.

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(40) Using the BDE(C$-$H) in *o*-cresol (370 kJ mol^{-1}, taken equal to that of toluene)[41] and the BDE(O$-$H) (355 kJ mol^{-1}, analogous to ref 19 with $\sigma_p^+(\text{methyl}) = -0.31$),[27] $\Delta_f H(o\text{-}CH_3-C_6H_4-O^\bullet)$ becomes 11.5 kJ mol^{-1} and $\Delta_f H(o\text{-}HO-C_6H_4-CH_2^\bullet)$ 26.5 kJ mol^{-1}. Thus addition of a hydrogen atom to **2** yields $\Delta_r H = -273$ kJ mol^{-1} (addition to C=CH_2) and $\Delta_f H = -258$ kJ mol^{-1} (addition to C=O).

(41) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744$-$2765.

(42) Substituting $k_1 = 0.36$ s^{-1} (903 K), $[o\text{-cresol}]_t = 0.5 \times 10^{-7}$ M, and $[\text{chroman}]_{t=0} = 32.4 \times 10^{-7}$ M in eq 5 yields $k_{\mathrm{RRD,exp}} = 12$ M^{-1} s^{-1}. For RRD the general Arrhenius parameters are $\log A = 8.6$ (per H) and $E_a = E_0 + 0.82 \times \Delta_r H$ (with $E_0 = 37.66$ kJ mol^{-1}).[43] The $\Delta_r H$ is 101 kJ mol^{-1} using $\Delta_f H$ of the compounds from refs 24 and 40. The rate equation becomes k_{RRD} (M^{-1} s^{-1}) = $1.2 \times 10^9 \exp(-121\ (\mathrm{kJ\ mol^{-1}})/RT)$, resulting in a predicted value $k_{\mathrm{RRD}} = 114$ M^{-1} s^{-1}.

(43) Savage, P. E. *Energy Fuels* **1995**, *9*, 590$-$598.

(44) For $C_6H_5CH_3 + H^\bullet \rightarrow C_6H_6 + {}^\bullet CH_3$, k (M^{-1} s^{-1}) = $1.55 \times 10^{10} \exp(-24.19\ (\mathrm{kJ\ mol^{-1}})/RT)$.[17] At 900 K in toluene/nitrogen, $[CH_4] = 7.3 \times 10^{-7}$ M.

(45) The rate parameters for Diels$-$Alder addition of an alkene to **2** can be derived for ethene but, in a first approximation, will also be applied to other alkenes with **2**. For the activation energy a value can be derived of $E_a(\text{DA}) = E_a(\text{retro-DA}) - \Delta_r H = 263 - 201 = 62$ kJ mol^{-1}. Assuming the same entropy change as for norbornene to cyclopentadiene and ethene (142 J mol^{-1} K^{-1})[17] a preexponential factor can be derived as 7.6×10^7 M^{-1} s^{-1}.

(46) (a) Ciriano Nogales, M. V.; Dorrestijn, E.; Mulder, P. To be published. For experimental details: (b) Arends, I. W. C. E.; Mulder, P. *Energy Fuels* **1996**, *10*, 235$-$242.

(47) Gaynor, B. J.; Gilbert, R. G.; King, K. D.; Harman, P. J. *Aust. J. Chem.* **1981**, *34*, 449$-$452.

(48) (a) Buxton, J. P.; Simpson, C. J. S. M. *Chem. Phys.* **1986**, *105*, 307$-$316. (b) Dolbier, W. R.; Frey, H. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1674$-$1676.

(49) Frey, H. M.; Hopf, H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2016$-$2019.

(50) AM1 calculations provide the C$-$H BDE in $CH_2=CH-C(=O)-\mathbf{H}$ (346 kJ mol^{-1}) and in $CH_2=CH-C(=CH_2)-\mathbf{H}$ (409 kJ mol^{-1}). These values, with the $\Delta_f H$ of 2,4,6-heptatrienal (40 kJ mol^{-1}),[24] yield a $\Delta_f H({}^\bullet C(=O)-CH=CH-CH=CH-C(=CH_2)^\bullet) = 359$ kJ mol^{-1}. Applying a $\Delta_f H$ of 66 kJ mol^{-1} for **2**[34] results in a BDE of 293 kJ mol^{-1}.

However, the stereospecificity of the reverse reaction suggests that a concerted pathway is operative. The barrier for rotation around the benzylic C−C bond, prior to the elimination of ethene, is too high to allow a retention of configuration. The product *o*-quinone methide (**2**) decomposes at high temperatures smoothly into benzene and CO, according to a concerted mechanism. It has been shown that *o*-quinone methide is very reactive toward alkenes (addition) and toluene (hydrogen transfer). Reverse radical disproportionation with toluene has been shown to be an important pathway in the formation of *o*-cresol. Since quinone methides are important intermediates in *e.g.* lignin liquefaction, the application of hydrogen donors is likely to be beneficial for the formation of usefull feedstock compounds.

Experimental Section

In this study two different experimental setups have been utilized. To investigate the (change in) product distribution of the thermal decomposition of **1** and **3**, an offline apparatus was used, while detailed kinetic parameters were determined using the online equipment.

Off-Line Experiments. This technique has been described before.[3] In short: a solution of the reagent in toluene (ca. 1000-fold excess) was lead by the carrier gas (molar ratio gas/reagent ca. 3500) through a heated quartz tubular flow reactor with an effective volume of 43.5 mL. Gaseous as well as liquid samples were obtained. To prevent any hold-up by condensation, all tubing was kept at 473 K. The gas samples were analyzed on a Packard 428A gas chromatograph (packed Carbosphere column 80/100 mesh) for CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6. Detection took place on a FID after methanization. The liquid samples were analyzed on a HP 5890A gas chromatograph (CP-Sil-5-CB capillary column, 50 m × 0.32 mm i.d., 0.4 μm film thickness) with H_2 as carrier gas and a FID detector. For identification a HP 5890 GC equipped with a mass spectrometric detector (HP 5972 MSD) was used. The residence times were between 7.7 and 9.0 s for the experiment with **1** and between 7.8 and 10.2 s for the experiments with **3**.

On-Line Experiments. The instrument and the analysis have been described before[3] but in contrast to former experiments, monitoring of data (GC signal, temperatures, flow, pressure) as well as controlling and regulating the equipment took place by software (Labview 3.1, HP GC Chemstation rev. A.03.02).[51] Nitrogen was used as carrier gas in case of the thermolysis of **1** and **2**. The residence times were between 2.9 and 4.0 s. When *cis*-2-butene was present during the thermolysis of **3** residence times were 3.5 to 5.5 s. On-line sampling took place on a HP 5890A series II gas chromatograph with He as carrier gas.

NMR Measurements. A ^{1}H-NMR spectrum of 200 scans in $CDCl_3$ was measured on a 300 MHz DPX300 from Bruker.

Chemicals. *o*-Hydroxybenzyl alcohol (Aldrich, 99%), chlorobenzene (Aldrich, 99.9%), *p*-chlorotoluene (Fluka, purum), toluene (Baker, p.A.), xylene (Baker, 98%), nitrogen (Air Products, ultrapure (on-line experiments), 99.9% (off-line experiments)), propene (Air Products, 99%), hydrogen (Air Products, 99.9%), *cis*-2-butene (Air Products, 99%), and methane (Air Products, 99.995%) were used as received. Chroman (**1**) was prepared according to the synthesis reported earlier.[52] The mass spectrum was in agreement with that from literature,[53] the GC-purity amounted to 98.5%.

***cis*-2,3-Dimethylchroman:** MS *m*/*z*: 162 (M^+, 63), 147 (29), 133 (100), 107 (74), 105 (43), 91 (44), 78 (48), 77 (42), 51 (29), 39 (34). NMR: δ 7.12−6.76 (m, 4H), δ 4.24 (dq, $J = 2.56$, 6.53 Hz, 1H), δ 2.95 (broad dd, $J = 5.75$, 16.31 Hz, 1H), δ 2.49 (broad dd, $J = 5.32$, 16.35 Hz, 1H), δ 2.09 (m, 1H), δ 1.28 (d, $J = 6.51$ Hz, 3H), δ 0.96 (d, $J = 9.97$ Hz, 3H).

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