Thermal Decomposition of 2,3-Dihydro-1,4-benzodioxin and 1,2-Dimethoxybenzene

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Rates and mechanisms of decomposition of 2,3-dihydro-1,4-benzodioxin (**1**) and 1,2-dimethoxybenzene (**27**) have been investigated in the gas phase near atmospheric pressure between 750 and 900 K in a tubular flow reactor in a large excess of radical trapping agents. The following rate expressions for decomposition have been determined: log k_t/s^{-1} (**1**) = 15.7 − (271 kJ mol^{-1}/2.303 *RT*); log k_t/s^{-1}(**27**) = 15.7 − (251 kJ mol^{-1}/2.303 *RT*). The main decomposition routes for **1** are the formation of *o*-benzoquinone (**2**) and 2-methyl-1,3-benzodioxole (**7**) through a biradical intermediate. The measured activation energy is 20 kJ mol^{-1} above the required C–O bond dissociation energy. Compound **2** rapidly loses CO to form cyclopenta-2,4-dien-1-one (**6**) which after dimerisation decomposes mainly into 3-phenylprop-2-enal (**12**) and indenols (**14**). The main product of the thermolysis of **27** is *o*-hydroxybenzaldehyde (**33**). The O-methyl bond is weakened by 16 kJ mol^{-1} compared to methoxybenzene as a result of the *o*-methoxy-substitution.

Knowledge of the strength of the phenoxy–R linkage is of both theoretical and practical importance. The variations in bond dissociation energy (BDE, E_d) as a function of R and substituents in the phenolic moiety enable a better insight into the fundamental role of these groups on this intrinsic property. On the other hand the thermal stability of various notorious environmental pollutants like dibenzodioxins and dibenzofurans appears to be related to the strength of the oxygen–carbon bridge in these molecules. In order to assess a bond strength from a unimolecular reaction in the gas phase, various experimental techniques, like shock-tube and very low pressure pyrolysis (VLPP), appeared to be successful. Stein[1] investigated the substituent effect on the phenoxy–methyl linkage in substituted methoxybenzenes using the VLPP method. It was shown that *ortho* and *para* substitution by a MeO group resulted in a weakening of 17 kJ mol^{-1}, which is consonant with results from related studies in the liquid phase using a photoacoustic technique.[2] This weakening can be rationalized by a strong interaction of the oxygen in the MeO-substituent with the unpaired electron in the product radical. Recently we have reported on the decomposition of methoxybenzene at atmospheric pressures in an excess of toluene. It was shown that when applying this toluene carrier method the BDE for PhO–CH_3 could be well established.[3]

These findings prompted us to study the rates and mechanisms of decomposition of various acyclic and cyclic aromatic ethers,[3–6] see Table 1. In this paper we report on the thermal decomposition of two compounds containing an *ortho* di-oxygen element: the cyclic 2,3-dihydro-1,4-benzodioxin (**1**), and the acyclic 1,2- (**27**) and 1,4-dimethoxybenzene (**35**).

The experiments were done in quartz tubular flow reactors near atmospheric pressure at temperatures between 750 and 900 K. Products were analysed using gas-chromatography and mass-spectrometry.

Results

2,3-Dihydro-1,4-benzodioxin (**1**).—Orientating thermolysis experiments in the off-line set-up (see Experimental section) between 770 and 900 K of **1** dissolved in excess benzene, yielded CO and ethene as the main products together with small quantities of indenols (two isomers) (**14**), 3-phenylprop-2-enal (*Z* and *E*) (**12**), styrene (**15**), 2-phenylprop-2-enal (**13**) and 2-methyl-1,3-benzodioxole (**7**). The overall mass balance was poor (less than 75%). Separate experiments were performed with methanol or toluene as the diluent, however no change in product pattern was observed. Only in case of methanol four additional unknown compounds with highest *m*/*z* = 87, 164, 178 and 178 were observed. In an excess of propene three isomers of methylated cyclohexadiene (**17**) and 3,4-dihydro-3-methyl-2*H*-1-benzopyran (**22**) (*m*/*z* = 148), *ca.* 4% of **17**, were also formed. All other products, except for **7**, CO and ethene, mostly disappeared depending on the propene excess. From Fig. 1, it can be concluded that the increase in the rate of formation of **17** is larger than the decrease of **12**, **14** and **15**. When applying a 67-fold excess of propene a substrate/product carbon mass balance of > 87% was observed.

Table 1 Bond dissociation energies of some aromatic ethers

Ether	E_d/kJ mol^{-1}	Ref.
PhO–Me	271, 273	1, 3
Ph–O–Ph	314	4
$PhCH_2$–OPh	218	4
PhO–$CHCH_2$	293	5
$\mathrm{CH[CH]_3CC{-}OCH_2CH_2}$	243	6
2-HOC_6H_4O–Me	241	1
PhO–Et	268	7
1,2-(Me–O)$_2C_6H_4$	253	1
1,4-(Me–O)$_2C_6H_4$	254	1

Several other products were formed in very small quantities (< 0.1%), like *o*-hydroxytoluene and unidentified compounds with *m*/*z* = 132, comprising *m*/*z* = 132, 103, 77 and 51 as the most abundant fragments. The two isomers of **12** (*m*/*z* = 131 > 132) could be identified by direct comparison of the retention time of the pure compounds. The presence of a phenolic group in the isomers of **14** was substantiated by derivatization of the OH group into the trimethylsilyl ethers.[8] Evidence of the phenolic character of the hydroxy group was found by extracting these compounds from the reaction mixture with an alkaline solution; a compound containing a hydroxy group attached to an aliphatic carbon, cannot be removed in such a way because of its high pK_a value. The ratio (1.8) of the isomers **14** is not changed during the course of the analyses as

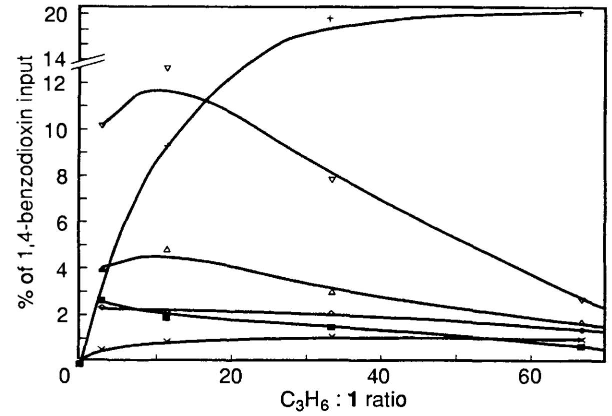


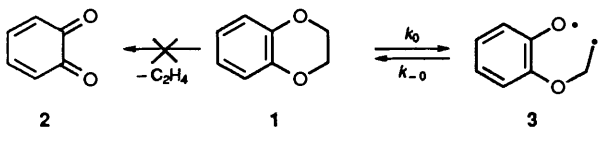
Fig. 1 Product profile as a function of the propene: 2,3-dihydro-1,4-benzodioxin ratio: +, **17**; ×, **22**; ◇, **7**; ▽, **14**; △, **12**; ■, **15**. At 873 K and 73% conversion.

was proved by lowering the injection port temperature of the gas chromatograph.[9] According to known mass spectra[10] the product (m/z = 136), formed at the same rate with or without propene, must be **7**. This was confirmed by GC retention time after synthesis of the compound.[11]

Rate measurements. Next on-line experiments (see Experimental section) with **1** and a large fixed propene excess (800 ×) were carried out. The overall aryl and oxygen mass balances were close to 100% throughout these experiments. Product distribution data are presented in Table 2. Due to poor GC resolution a few compounds, like product **12**, were not quantified. The main emphasis for these experiments was to monitor accurately the rate of disappearance of **1** as a function of the reaction temperature.

From Fig. 2 it can be seen that the main products like CO and the methylcyclohexadienes (**17**) increase with increasing conversion of **1**. Especially the CO production appears to be equal to almost twice the amount of **1** which disappeared (meaning that for every mol of **1** converted, 2 mol of CO are formed). The ethene formation in the higher temperature region is somewhat obscured by the pyrolysis product (ethene) of propene. Blank runs with propene only showed that this reaction sets in at 800 K. Also in the high temperature region the methylcyclohexadienes are unstable and react further (to *e.g.* toluene). The cluster of not separately quantified compounds (see Table 2) comprises **12**, **13** and **15**.

For the calculation of the Arrhenius parameters of the decomposition of **1** a first-order behaviour is assumed in our tubular flow reactor (Scheme 1). The overall unimolecular rate



Scheme 1 Homolysis of the C–O linkage in **1**

constant, k_t (s^{-1}), is derived according to: $\ln (C/C_0) = -k_t \times \tau$ [eqn. (1)]; with τ = residence time (s) and C and C_0 the final and initial concentration respectively. The C/C_0 ratio is determined in two different ways. From 773 to 843 K C/C_0 was calculated according to $C/C_0 = 1 - [\Sigma(\text{products})/C_0]$ [eqn. (2)] and from 848 to 903 K the input : output ratio of substrate was used (Fig. 3). This method yielded the most consistent and accurate results. A plot of $\log k_t$ *vs.* 10^3 K/T is presented in Fig. 4. The Arrhenius expression $\log k_t = \log A - E_a/2.303\,RT$ [eqn. (3)], as a result of data linear regression analysis was found to be:

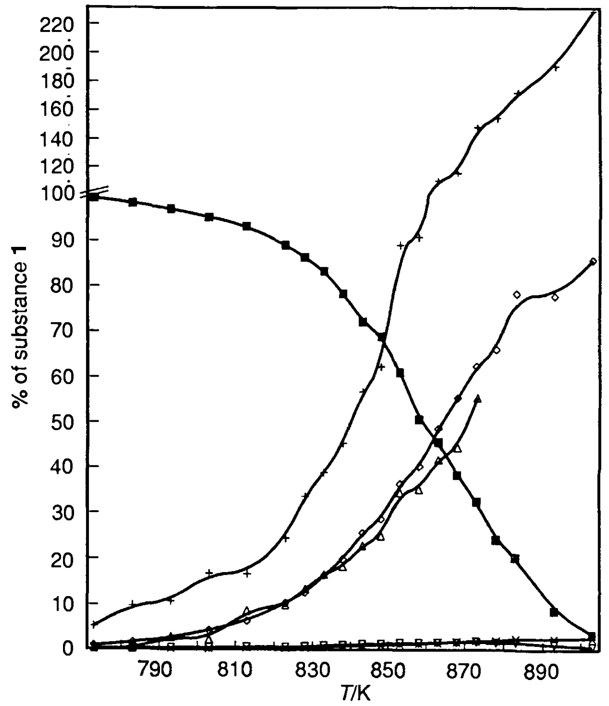


Fig. 2 Product and substrate profile in % of substrate **1** intake: ◇, **17**; and decomposition products of **17**; ×, **7**; +, CO; ▽, **22**; △, C_2H_4; ■, **1**.

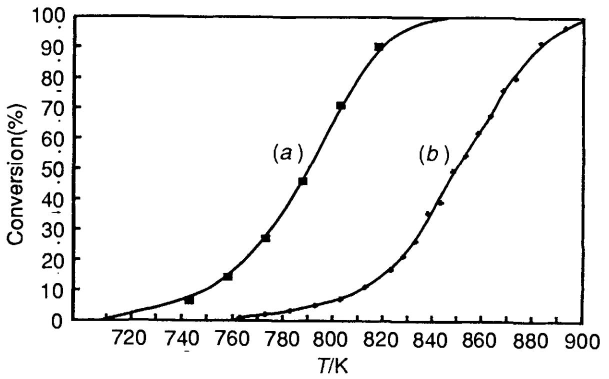


Fig. 3 Conversion of **1** (*b*) and **27** (*a*) (average residence time 4 s)

$$\log k_t/\mathrm{s}^{-1}\ (\mathbf{1}) = 15.7 \pm 0.2 - (271 \pm 3\ \mathrm{kJ\ mol^{-1}}/2.303\ RT)$$
$$(r^2 = 0.9975)$$

1,2-Dimethoxybenzene (**27**).—The stable products of the decomposition of **27** were methane, phenol (**31**) and *o*-hydroxybenzaldehyde (**33**). *p*-Fluorotoluene served as a radical scavenger to prevent induced decomposition. To verify if the scavenging efficiency was sufficient several additional experiments were carried out. In toluene carrier experiments, the only reactive species that might induce the decomposition of substrate are benzyl radicals. In fact bibenzyl (recombination of two benzyl radicals) is the main product in these thermolysis experiments. By extending the residence time the concentration of benzyl relative to other compounds will increase and thereby possibly accelerate the unwanted bimolecular interaction. Besides extending the residence time (molarity was kept the same) other experiments were carried out in which the concentration of substrate was reduced. In both cases the reaction rate constant of decomposition did not change significantly, nor did a change in products occur. This tallies with the assumption that the contribution of induced decomposition is negligible.

Product formation became noticeable at 730 K (τ = 3.6 s).

Table 2 Gas phase thermal decomposition of 2,3-dihydro-1,4-benzodioxin

	T/K																			
	773	783	793	803	813	823	828	833	838	843	848	853	858	863	868	873	878	883	893	903
Residence time/s	4.4	4.3	4.3	4.2	4.1	4.1	4.1	4.0	4.0	4.0	4.0	4.0	3.9	3.9	3.9	3.9	3.8	3.8	3.8	3.7
Intake[a] dihydrobenzodioxin	26	25	23	22	23	22	22	20	18	17	17	17	17	16	16	16	16	15	16	16
Conversion (%)	0.8	1.9	3.2	5.0	7.1	11.2	13.9	17.0	21.9	28.1	31.4	39.2	49.6	54.6	62.0	67.7	76.1	80.0	91.6	96.8
Product[b]																				
cyclohexadiene **17**[c]	174	333	557	880	1 415	2 205	2 614	3 084	3 465	4 085	4 500	5 342	5 818	6 494	6 976	7 643	7 810	8 783	7 984	7 778
decomp. prod. of **17**	—	—	—	—	—	—	154	201	122	287	447	748	998	1 200	1 581	2 087	2 511	3 149	4 669	5 800
methylbenzodioxole **7**	3	6	9	17	36	62	67	91	103	129	132	168	188	215	235	276	285	339	354	371
22	23	24	35	52	75	93	108	147	156	174	186	215	225	219	222	234	211	210	142	73
indenols **14**[d]	—	—	—	—	—	2	6	13	16	18	19	53	66	84	99	126	132	181	189	203
minor/unidentified[e]	17	121	131	128	124	90	155	139	136	154	163	214	316	329	463	586	678	778	1 196	1 727
CO	1 284	2 352	2 379	3 549	3 786	5 271	7 466	7 903	8 253	9 780	10 481	14 993	15 446	17 402	17 788	23 037	24 068	26 131	30 933	36 189
ethene[f]	—	—	561	423	1 932	2 107	2 938	3 327	3 290	3 891	4 305	5 784	5 955	6 614	6 865	8 646	*g*	*g*	*g*	*g*

[a] Intake/10^{-6} mol dm^{-3}, together with N_2 = 1846, C_3H_6 = 12 615 and CO_2 = 160 (10^{-6} mol dm^{-3}). [b] Products in 10^{-9} mol dm^{-3}. [c] Sum of three methylated isomers. [d] Sum of two isomers. [e] See text. [f] Corrected for propene decomposition products. [g] No accurate results. — Below detection limit ($< 10^{-9}$ mol dm^{-3}).

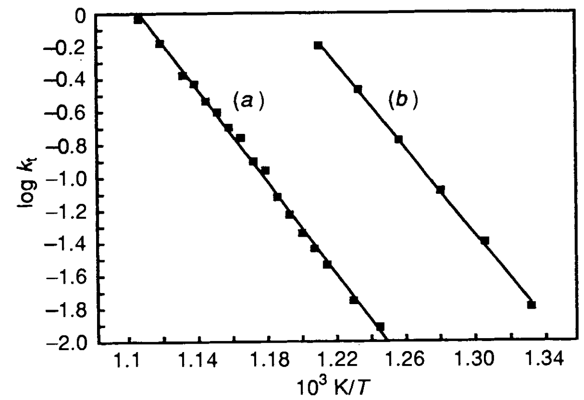


Fig. 4 Arrhenius plot of **1** (*a*) and **27** (*b*)

No difference in the formation of products was noticed between off-line and on-line experiments. Product distribution data are presented in Table 3. These thermolysis experiments were performed in the presence of methoxybenzene. Since rate parameters of the decomposition of this compound are well established it serves as an internal standard to calibrate the temperature of the reactor. The amount of phenol in Table 3 has been adjusted for the additional phenol formation from methoxybenzene.

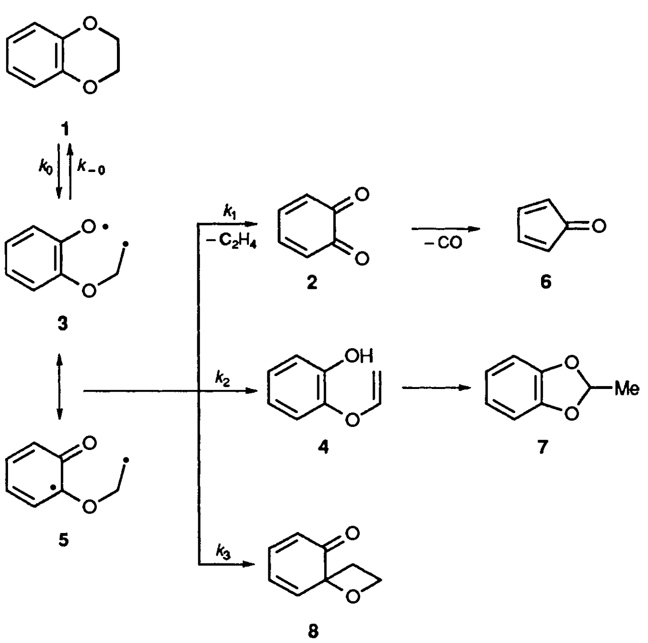
Rate measurements. The unimolecular overall rate constant, k_t (s^{-1}), was calculated as outlined above [according to eqn. (1)], based on conversion of substrate (determined by CO_2 acting as an internal standard). The conversion of dimethoxybenzene (**27**), and the Arrhenius plot found, are presented in Figs. 3 and 4. The rate expression found for the disappearance of **27** is:

$$\log k_t/s^{-1}(\mathbf{27}) = 15.7 \pm 0.3 - (251 \pm 4\ \text{kJ mol}^{-1}/2.303\ RT) \quad (r^2 = 0.9989)$$

1,4-*Dimethoxybenzene*.—The main (stabile) product of decomposition is *p*-benzoquinone (**37**) with a yield ranging from 97 to almost 100%. At higher substrate concentrations 4-methoxybenzaldehyde and an unknown product (m/z = 196) were formed.

Discussion

2,3-*Dihydro*-1,4-*benzodioxin*.—The thermolysis of **1** obeys the unimolecular rate expression of $\log k_t/s^{-1} = 15.7 \pm 0.2 - (271 \pm 3\ \text{kJ mol}^{-1}/2.303\ RT)$; these overall parameters are the basis for our mechanistic interpretation of the decomposition of **1**. The primary product of decomposition is ethene. On an *a priori* basis, the formation of ethene can be envisaged by a molecular concerted pathway (*i.e.* a retro-Diels–Alder reaction) or *via* a biradical intermediate process (see Scheme 1). The kinetic distinction between these two processes is found in the magnitude of the preexponential factor and especially the activation barrier. For example, the decomposition of cyclohexene to ethene and butadiene requires an overall activation energy of 278 kJ mol^{-1}.[12] The energy needed for the rupture of a carbon–carbon bond in cyclohexene to form the corresponding biradical amounts to 318 kJ mol^{-1}, and therefore this reaction must proceed in a concerted fashion. In general, when the observed activation energy exceeds the dissociation energy of the bond of interest, this type of decomposition reaction is likely to follow a biradical pathway. Hence, in our case the value of the aliphatic carbon–oxygen bond strength in **1** is necessary to assess the reaction mode.



Scheme 2 First steps of the reaction mechanism of thermal decomposition of **1**

From literature data[7] it can be derived that the BDE for the ethyl–oxygen linkage in ethoxybenzene is 268 kJ mol^{-1} (Table 1). According to our rate data on the decomposition of 1,2-dimethoxybenzene (*vide infra*), *ortho* substitution by a methoxy group weakens the carbon oxygen (in this case of the O–CH_3) bond by 16 kJ mol^{-1}. Without any additional ring strain in 2,3-dihydro-1,4-benzodioxin a carbon–oxygen BDE of 252 kJ mol^{-1} can be estimated. Taking into account the measured activation energy of 271 kJ mol^{-1} and together with $\Delta C_p \simeq 0$ for **1** → **3**, it is concluded that the thermolysis of **1** starts with the reversible C–O bond cleavage. Note, that an additional activation energy of *ca.* 19 kJ mol^{-1} is required above the intrinsic BDE (*vide infra*). A similar phenomenon has been observed for the decomposition of tetralin.[13]

The biradical **3**, and its resonance structure **5**, can react further by three possible routes (see Scheme 2), apart from the reversal to **1**. The first route is the formation of *o*-benzoquinone (**2**). After ring opening of **1** the intermediate radical **3** will split off a molecule of ethene to form **2** as depicted in Scheme 2. Since **2** was not found in the product mixture, thermal decomposition into CO and cyclopenta-2,4-dien-1-one (**6**) must be a rapid process. The C–C bond strength between the two carbonyl-elements is estimated to be *ca.* 170 kJ mol^{-1}. Moreover, the heat of formation of both **2** and its decomposition products dictate that the overall reaction is exothermic by 39 kJ mol^{-1},* making a direct elimination of CO to give **6** under these conditions feasible. The low concentration of **2** is further substantiated by the observation that upon addition of a large excess of methanol to the reaction mixture, assuming an equilibrium between **2** and the open ketene structure, the di-ester **10** could not be detected by GC–MS (Scheme 3). Furthermore in the kinetic experiments with a large excess of propene, 2-methyl-2,3-dihydro-1,4-benzodioxin (**9**), which could arise through a (formal) Diels–Alder reaction of **2**, could not be detected by GC–MS either (see Scheme 3).

Without propene the dimer **11** of **6** is likely to be produced which subsequently decomposes and rearranges to yield the observed products, **12**–**15**. If propene is added to the reaction mixture it appears to act as a trapping reagent for **6**; this should give the corresponding Diels–Alder product, 5-methylbicyclohept-2-en-7-one (**16**) (Scheme 4).

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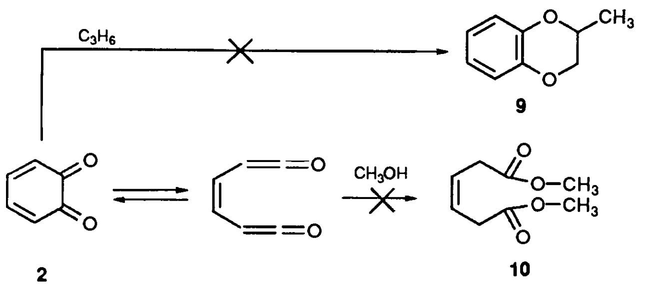
* According to the NIST database[15] at 298 K, $\Delta H_f^\circ(\mathbf{2}) = -105$, $\Delta H_f^\circ(\mathbf{6}) = -34$ and $\Delta H_f^\circ(CO) = -111$ kJ mol^{-1}.

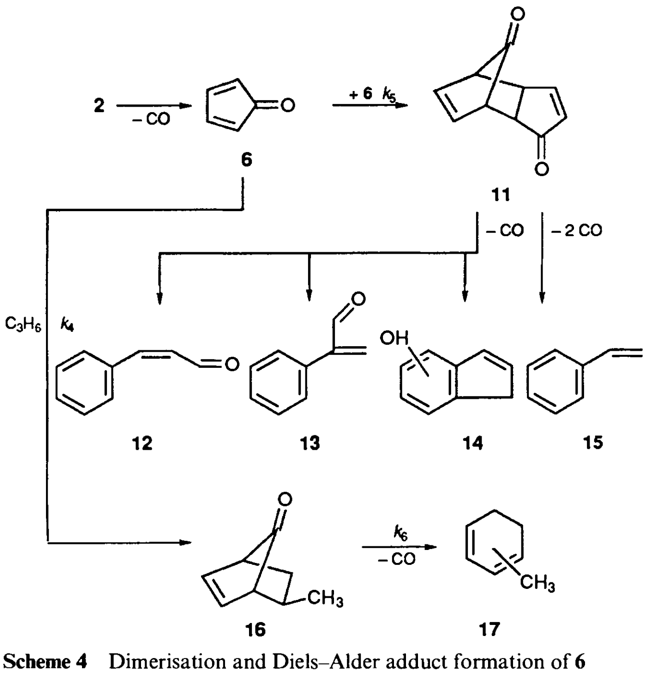
Table 3 Gas phase thermal decomposition of 1,2-dimethoxybenzene (**27**) and methoxybenzene

	T/K					
	751	766	781	796	811	826
Residence time/s	3.9	3.8	3.7	3.7	3.6	3.5
Intake[a]						
1,2-dimethoxybenzene **27**	43.7	54.9	45.7	52.7	15.8	32.6
methoxybenzene	21	20	20	19	19	19
Conversion (%)						
1,2-dimethoxybenzene **27**	6.0	14.0	26.5	45.7	70.4	89.1
methoxybenzene	0.3	0.6	1.3	2.8	5.8	11.4
Products[b]						
phenol **31**[c]	—	1.48	2.65	4.17	2.57	7.64
hydroxybenzaldehyde **33**	2.62	6.21	9.44	19.93	8.57	21.37
phenol **31**[d]	0.05	0.12	0.26	0.58	1.09	2.15
CH_4:CO ratio[e]	—	—	4.22	3.97	4.22	3.23
Product ratio **33**:**31**[c]	—	4.2	3.6	4.8	3.3	2.8
Product ratio (**33** + **31**):**31**[c]	—	5.20	4.56	5.77	4.33	3.80

[a] Intake/10^{-6} mol dm^{-3}, together with N_2 = 2200, CO_2 = 245, *p*-$FC_6H_4CH_3$ = 500; *P* = 1.45 atm. [b] Products/10^{-6} mol dm^{-3}. [c] Phenol from **27** = total phenol observed—converted methoxybenzene. [d] Phenol from converted methoxybenzene. [e] Corrected for CH_4 formed out of *p*-$FC_6H_4CH_3$, at 751, 766 K; CO below detection limit (< 10^{-9} mol dm^{-3}). — Below detection limit (< 10^{-9} mol dm^{-3}).



Scheme 3 Possible channels to trap *o*-benzoquinone



Scheme 4 Dimerisation and Diels–Alder adduct formation of **6**

The product **16** is also thermally unstable and is converted into CO and **17**.[14] This decarboxylation is fast enough to prevent the reversal of the Diels–Alder reaction of **6** with propene. The consequence is an almost irreversible conversion of **6** into CO and a mixture of methylcyclohexadienes. It is of interest to analyse the rates of the reactions displayed in Scheme 4. Little is known about the exact magnitude of the Diels–Alder reaction rates of **6**. The Diels–Alder reaction rate parameters (and also for the reverse process) for similar reactions *i.e.* cyclopentadiene and ethene are known,[16] as well as the rate parameters for the decomposition of bicyclohept-2-en-7-one.[14] If these parameters are also valid for the sequence **6**→**16**→**17** the irreversible conversion of **6** into **17** is being underscored. The concentration of **6** (> 10^{-6} mol dm^{-3}) predicted by this model however is too high according to experimental evidence. Thus, the Diels–Alder addition of propene to **6** must be faster. According to Gavina *et al.*[17] the rate constants for the Diels–Alder addition of **6** to several alkenes vary from 0.6 to 6.7 × 10^{-4} dm^3 mol^{-1} s^{-1} in the liquid phase at 373 K. If this range would also hold for the gas phase and suggesting a log *A* factor of 7.6,[16] then k_4 would amount to *ca.* 600 dm^3 mol^{-1} s^{-1} at 850 K, leading to a computed value for **6** of 1.76 × 10^{-7} mol dm^{-3}. From Table 2 it can be inferred that around 6% of the condensation products stem from processes other than reaction of **6** with propene.

The formation of indenols is likely to proceed through dimerization *via* a Diels–Alder type reaction and consequently a rate constant (k_5) of at least 4 × 10^8 dm^3 mol^{-1} s^{-1} is required. Although such a high rate constant seems unrealistic, it should be pointed out that liquid phase studies also revealed an unexpectedly high dimerization rate constant relative to those with alkenes.[17]

In the kinetic experiments the organic products are methylcyclohexadiene isomers and 2-methyl-1,3-benzodioxole (**7**). Under comparable reaction conditions, but in the absence of propene, only similar yields of **7** were obtained. Therefore, another product channel is operative starting from the biradical intermediate.

Besides ethene elimination to give **2**, at first sight a second route from the biradical **3** would be an internal disproportionation, as is also observed in the pyrolysis of other cyclic ethers,[4] to form *o*-vinyloxyphenol (**4**) (see Scheme 2). However, this product is not observed, instead **7** is found in the product mixture. Product **7** appeared to be stable under the reaction conditions used. This result is rather surprising, because due to the additional strain in the five membered ring a C–O BDE weakening of *ca.* 34–35 kJ mol^{-1} in **7** compared to **1** can be estimated,* so thereby lowering its thermal stability. To verify if

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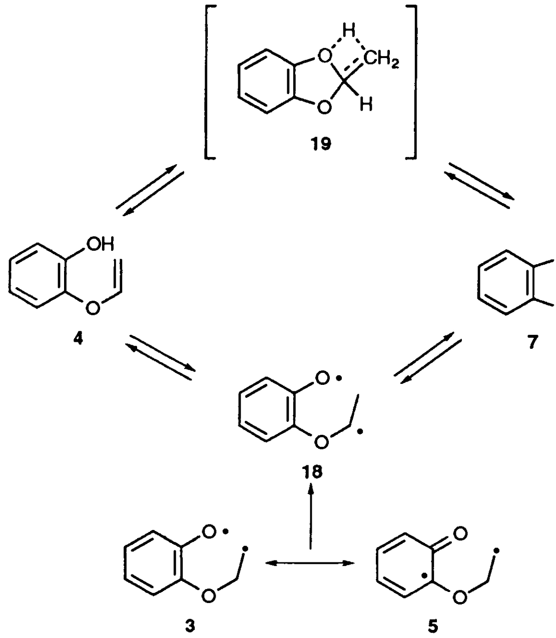
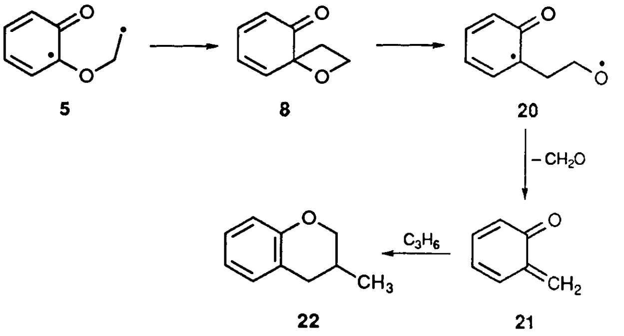
* ΔH_f° of **3** is estimated as 47 kJ mol^{-1},[15] change from a primary to a secondary alkyl radical involves 16 kJ mol^{-1},[15] therefore ΔH_f°(**18**) (see Scheme 5) = 31 kJ mol^{-1}. Together with an estimated ΔH_f° of (**7**) of – 186 kJ mol^{-1},[15] a C–O BDE of 217 kJ mol^{-1} in **7** is found; 35 kJ mol^{-1} weaker than in **1**.

indeed **7** is stable under our reaction conditions the compound was synthesized[11] and thermolysed. These additional experiments revealed no conversion of **7** at 845 K and $\tau = 5.4$ s, whereas under the same conditions 38% of **1** was already decomposed. The decomposition of **7** starts at 880K. At 933 K a conversion of 28% is observed, with CO and C_2H_4 as the main products. Only small amounts of **4**, but no significant other organic products were detected by GC–MS. Moreover **1** was not observed, implying that the reverse reaction of **7** to **1** does not occur. Thus, the formation of **7** can, if **4** is the precursor molecule, be envisaged by two different ways, as outlined in Scheme 5. First, the molecular concerted way, which involves a four-centre cyclic transition state **19**. Decomposition of, for example, phenyl *tert*-butyl ether[18] into phenol and isobutene, proceeds through a similar transition state. Under typical thermolysis conditions this bimolecular reverse reaction will be too slow to compete, however in our case the corresponding unimolecular intramolecular addition seems feasible. The second route may be reverse disproportionation to produce the biradical intermediate **18** through a seven-membered transition state (see Scheme 5). Whatever the real mechanism(s) might be, with only equilibrium considerations a substantial amount of **4** relative to **7** can be predicted. A more likely pathway is the direct isomerisation of **3** (and **5**) into **18** (see Scheme 5). This 1,2-H-shift rearrangement is slightly exothermic (16 kJ mol^{-1}). From our kinetic analysis (k_{t2}, *vide infra*) of the decomposition channels of **1**, it can be inferred that the formation of **7** from **1** requires an additional energy of *ca.* 34 kJ mol^{-1} (above the C–O BDE); which might be identified as the activation barrier for this 1,2-H-shift reaction. This also explains the unexpected stability of **7** because after ring opening another 50 kJ mol^{-1} is necessary to convert the apparent biradical **18** into **3** after which degradation into C_2H_4 and CO will take place.



Scheme 5 Formation of 7

The third possible route *via* the biradical **5**, a resonance structure of **3** (see Scheme 2) involves the formation of an oxetane intermediate **8**. Ring closure to form the four-membered ring will be slow compared to splitting producing ethene and **2**.[19a] Therefore, this route is likely to have only a minor contribution to thermal decomposition of **1**. Since the oxetane can only exist as an intermediate, its thermolysis involves both C–O and C–C bond cleavage: the ratio of the rates will be around C–O : C–C = 0.7 at 850 K.[19b] Breaking the C–O bond forming **20** may yield **21** after elimination of CH_2O (see Scheme 6). However, this compound could not be observed as a stable end product in our experiments. Only in the presence of a large excess of propene, 3,4-dihydro-3-methyl-2*H*-1-benzopyran (**22**) was found (yield less than 0.5% based on converted **1**), suggesting that the route of formation involves **21** as a precursor. It is of interest to note that addition of propene to the intermediate **21** now appears feasible (see Scheme 6) which can be rationalized by the higher thermal stability of **21** compared with benzoquinone (see Scheme 3).



Scheme 6 Oxetan intermediate route of the reaction mechanism of thermal decomposition of **1**

The separate kinetic expressions for formation of ethene and 2-methyl-1,3-benzodioxole (**7**) can be derived accepting that these compounds stem from the same biradical intermediate. The rate constants k_0, k_{-0}, k_1, k_2 and k_3 are depicted in Scheme 2. Assuming steady state conditions and with k_t being the overall and measured rate of disappearance of the substrate, expression (4) is found. Because it is impossible to calculate k_1,

$$k_t = [k_0 \times (k_1 + k_2 + k_3)]/(k_{-0} + k_1 + k_2 + k_3) \quad (4)$$

k_2 and k_3 directly, the overall rate constants (k_{t1} and k_{t2}) of **2** and **7** formation are defined as eqns. (5) and (6). Due to the

$$k_{t1} = [(\sum\text{products} - 7)/(\sum\text{products})] \times k_t \quad (5)$$

$$k_{t2} = [7/(\sum\text{products})] \times k_t \quad (6)$$

thermal instability of **22**, k_{t3} cannot be derived. The term 'Σproducts' includes: methylcyclohexadienes (**17**), decomposition products of (**17**), 2-methyl-1,3-benzodioxole (**7**), 3,4-dihydro-3-methyl-2*H*-1-benzopyran (**22**), indenols (**14**) and the minor and/or unidentified products (see Table 2). With the data regression analysis treatment, the following rate expressions for the two decomposition channels (Fig. 5) are obtained.

$$\log k_{t1}/\text{s}^{-1} = 15.6 \pm 0.2 - [(270 \pm 3\ \text{kJ mol}^{-1})/2.303\ RT] \quad (r^2 = 0.9974)$$

$$\log k_{t2}/\text{s}^{-1} = 15.0 \pm 0.3 - [(286 \pm 5\ \text{kJ mol}^{-1})/2.303\ RT] \quad (r^2 = 0.9962)$$

These rate constants imply that less than 5% of **1** is converted into **7** over the temperature range employed in this study.

Tsang *et al.*[13] studied the homogenous decomposition of tetralin (**23**) in the temperature range 1000–1400 K in single pulse shock tube experiments. After the initial reversible C–C bond cleavage the tetraline biradical (**24**) is converted into benzocyclobutene (**25**) and *o*-allyltoluene (**26**) (Scheme 7). The proposed reaction modes appear to be quite similar with those advanced for the decomposition of **1**. By a computing method,

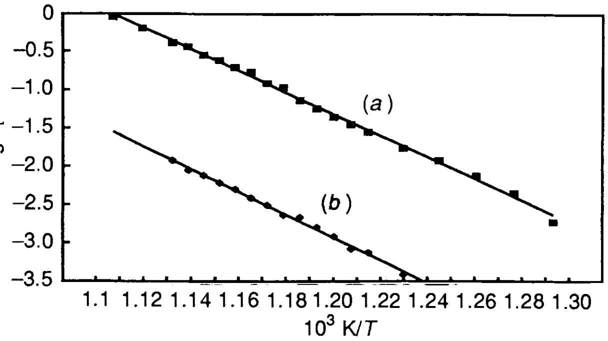
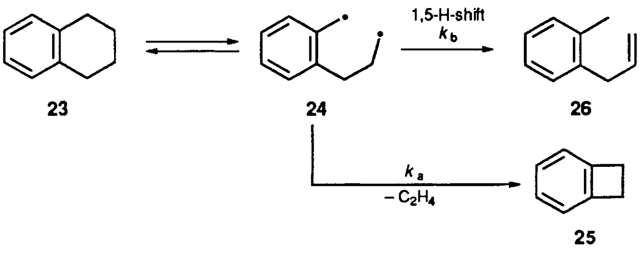


Fig. 5 Arrhenius plots of k_{t1} (*a*) and k_{t2} (*b*)



Scheme 7 Rate determining steps in tetralin thermal decomposition

in analogy with eqns. (5) and (6), Tsang *et al.* found the following rate expressions for the formation of **25** and **26**.

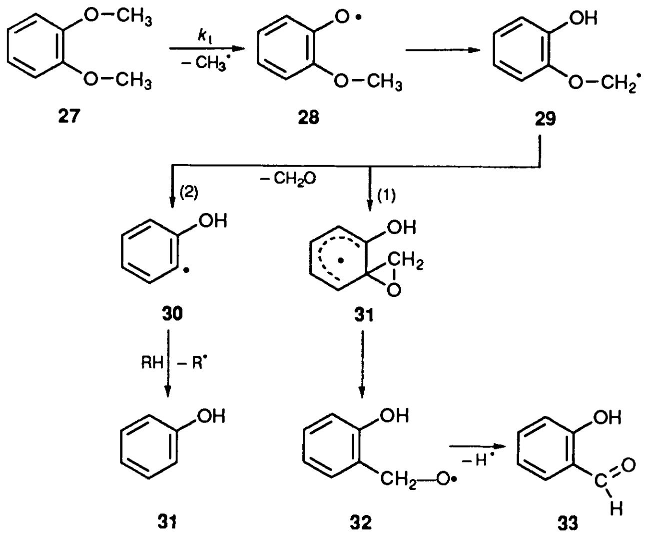
$$\log k_{ta}/s^{-1} = 15.5 - (333\ \mathrm{kJ\ mol^{-1}}/2.303\ RT)$$

$$\log k_{tb}/s^{-1} = 15.1 - (334\ \mathrm{kJ\ mol^{-1}}/2.303\ RT)$$

First, it is noted that the overall activation energy is about 30 kJ mol^{-1} higher than needed to break the C–C bond, while for the overall rate of conversion of **1** an excess energy of *ca.* 20 kJ mol^{-1} was found. Secondly, the difference in activation energies between the two internal reaction modes is very small, which has been rationalized by suggesting that the twist motion in the biradical prior to the elimination of ethene will also bring the β-hydrogens into a favourable configuration for the internal disproportionation. Therefore, the extra increment in activation energies must be related to the internal barrier of rotation. This implies that the elimination of ethene has essentially no activation energy. According to EPR studies[20] the delocalisation of the free electron in benzylic type radicals into the aromatic nucleus is around 40%, accordingly the initially formed 1,6-singlet-biradical should be considered as a 1,4 radical entity. The β bond in such an intermediate is extremely weak and will not contribute to the activation energy. The degree of delocalisation of the free electron into the aromatic ring in the biradical formed from **1** is even more pronounced. Based on product studies we have shown,[3] that *ca.* 90% of the free electron in the phenoxyl radical is situated on the *ortho* and *para* positions of aromatic ring. Replacing an *ortho* hydrogen by a substituent containing oxygen (*e.g.* OH, OCH_3) may reduce the spin density on the O even more. Moreover with Raman resonance spectroscropy it has been shown that the C–O bond in the phenoxyl radical is very close to a double bond.[21] Thus, the best representation of **3** is probably structure **5** (see Scheme 2). In contrast with the tetralin study, it was possible to demonstrate the presence of this 1,4 biradical, because it manifests itself as the precursor for compound **22** as shown in Scheme 6.

1,2-Dimethoxybenzene.—The observed activation energy of 251 kJ mol^{-1} can be used to derive the C–O bond dissociation energy in **27**. However, this number needs to be corrected according to: $E_d = E_a + RT$ [eqn. (7)]; yielding at the mean temperature of 788 K E_d(C–O) = 257 ± 4 kJ mol^{-1}. Within uncertainties and without C_p correction, this value is in excellent agreement with a BDE of 253 kJ mol^{-1} found by Stein *et al.*[1] It also shows that compared to methoxybenzene, the C–O BDE is lowered by 16 kJ mol^{-1} due to the second methoxy group. The preexponential factor is again commensurate with our earlier work on the thermolysis of methoxybenzene (log A = 15.3); due to the statistical correction a value of 15.6 would be expected, and the experimental result of 15.7 is, within experimental error, identical.

After losing a methyl radical due to homolytic cleavage of the C–O bond the methoxyphenoxy radical (**28**) is converted as a result of internal H-abstraction. No 2-hydroxymethoxybenzene will be formed, because the rate of the bimolecular H-abstraction from *p*-fluorotoluene is too slow. The newly formed radical **29** decays through two channels (Scheme 8). The major channel includes a rate determining 1,2-aryl-shift, with the parameters suggested by Mulcahy *et al.*[22] to be: log $k_{(\mathrm{channel\ 1})}/s^{-1} = 12.5 - (88\ \mathrm{kJ\ mol^{-1}}/2.303\ RT)$. The benzoyl radical **32** formed due to the 1,2-aryl-shift decomposes quickly by losing a hydrogen atom. According to the rate constants advanced by Brezinsky,[23] $\log k/s^{-1} = 13.9 - (72\ \mathrm{kJ\ mol^{-1}}/2.303\ RT)$, for loss of a hydrogen atom to form the main product **33**, its rate is a hundred times faster (at 820 K) than eliminating a molecule of formaldehyde. The second reaction channel is the main source of phenol through decomposition of **29** to give the *o*-hydroxyphenyl radical (**30**) and formaldehyde. Phenol arises by H-abstraction from the carrier agent. The rate constant of channel 2 can now be calculated by using the measured product ratio **33**:**31**, see Table 3. With a log A value of 14[*] the mean activation energy for channel 2 amounts to 119 kJ mol^{-1}. The enthalpy change in the process of forming **30** from **29** can be estimated[†] as 95 kJ mol^{-1} so that the E_a for the



Scheme 8 Proposed reaction mechanism of thermal decomposition of compound **27**

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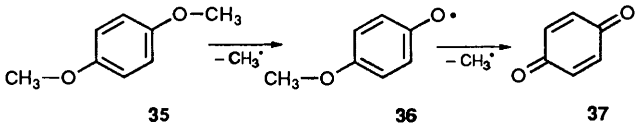
[*] Brezinsky[23] found log A = 14 for the process of losing formaldehyde from compound **32**, in the excited state. Channel 2 is likely to have comparable entropy difference.

[†] ΔH_r for a complete process, $PhO{-}CH_2^• \rightarrow Ph^• + CH_2O$ (*a*), can more easily be estimated. $\Delta H_f^\circ(CH_2O) = -109$ kJ mol^{-1}, (ref. 15), $\Delta H_f^\circ(Ph^•) = 329$ kJ mol^{-1} (ref. 15), but $\Delta H_f^\circ(PhO{-}CH_2^•)$ is estimated from the following process: $PhO{-}CH_3 \rightarrow PhO{-}CH_2^• + H$ (*b*), $\Delta H_r(b) = 418$ kJ mol^{-1} (ref. 15), $\Delta H_f^\circ(H) = 218$ kJ mol^{-1} (ref. 15) and $\Delta H_f^\circ(PhO{-}CH_3) = -75$ kJ mol^{-1} (ref. 15), so $\Delta H_f^\circ(PhO{-}CH_2^•)$ must be 125 kJ mol^{-1}. Thus, $\Delta H_r(a) = 329 - 109 - 125 = 95$ kJ mol^{-1}.

reverse reaction, that is the addition of a phenyl radical to the oxygen site of formaldehyde, will amount to (119 − 95 − *RT*) 17 kJ mol^{-1}. Only a few examples[15] can be found in the literature pertaining to the addition of radicals to the oxygen atom of formaldehyde. Because of the weak C–H bond, H-abstraction is found to be the major reaction mode. Furthermore, the additions will become reversible above *ca.* 350 K even when the addition process involves the formation of a strong bond.

As can be seen from Table 3, only CO was observed, while the oxygen mass balance remains almost 100% for the experiments. Formaldehyde, when formed under our reaction conditions, is probably converted very rapidly into CO. A rationale might be the hydrogen abstraction by benzyl radicals, followed by loss of H from the formyl radical ($CH_2O + p\text{-}FPhCH_2^{\bullet} \rightarrow {}^{\bullet}CHO + p\text{-}FPhCH_3$, ${}^{\bullet}CHO \rightarrow CO + H$) which are present in the reaction mixture at a concentration level of *ca.* 10^{-8} mol dm^{-3}. Benzaldehyde is likely to decompose like formaldehyde, however *o*-hydroxybenzaldehyde (**33**) may be regenerated as a result of an internal H-abstraction forming a phenoxy radical followed by a H-abstraction from the carrier. The methyl radicals formed in the decomposition of **27** will end up as CH_4 ($CH_3^{\bullet} + p\text{-}FPhCH_3 \rightarrow CH_4 + p\text{-}FPhCH_2^{\bullet}$), the ratio CH_4:CO should parallel that of (**33** + **31**):**31** according to Scheme 8. From Table 3 it can be inferred that is in general the case with the exception of the first two experiments, where the conversion of CH_2O into CO is supposedly incomplete.

1,4-*Dimethoxybenzene.*—Analogous to 1,2-dimethoxybenzene, the rate determining step of decomposition is the homolytic cleavage of the CH_3–O bond. No accurate thermodynamic parameters can be derived without kinetic measurements. By comparison with the rate of decomposition of **27** the C–O bond weakening effect due to the *p*-MeO substituent is, within experimental uncertainty, the same. The 4-methoxyphenoxyl radical (**36**) could react with *p*-fluorotoluene to form 4-methoxyphenol ($4\text{-}MeOPhO^{\bullet} + p\text{-}FPhCH_3 \rightarrow 4\text{-}MeOPhOH + p\text{-}FPhCH_2^{\bullet}$) or split off a second methyl radical to produce *p*-benzoquinone (**37**) (see Scheme 9). The results show that only **37** arises. The rate constant for H-abstraction will be around $\log k/dm^3\ mol^{-1}\ s^{-1} = 8.5 - (60\ kJ\ mol^{-1}/2.303\ RT)$,[24] which results in $k \times [p\text{-}FPhCH_3]$ of *ca.* 17 s^{-1} at 793 K. The loss of the second methyl has an overall endothermicity of *ca.* 150 kJ mol^{-1}, and even with log *A* as low as 14, the rate constant at 793 K will be above 10^4 s^{-1}, and therefore phenol formation under these conditions is not observed.



35 **36** **37**

Scheme 9 Proposed reaction mechanism of thermal decomposition of compound **35**

Experimental

In this study two different experimental set-ups have been utilised.

Off-line experiments. This technique was used to obtain a general impression of the behaviour of the compounds of interest under various conditions. One experiment was carried out at a specific reaction temperature (mostly for 30 min); and reaction samples collected and analysed.

The apparatus consists of a quartz tubular flow reactor, effective volume 35 cm^3, mounted in an electrically heated oven, controlled by a temperature regulator. To prevent condensation, heating tape was used to heat the in- and out-put lines of tubings of the reactor. Gases were introduced by calibrated flowmeters and the diluted substrate was added with a motor driven syringe. The total gas flow could be checked at the end of the apparatus with a soap-film-burette. A mercury filled vessel acted as a safety-valve.

From these experiments both liquid and gaseous samples were obtained. First, gas samples were collected with a gas bulb and analysed on a Packard 428A gas chromatograph (packed Carbo plot 007 column) for CO, CO_2, CH_4, C_2H_2, C_2H_4 and C_2H_6. Detection took place on a FID after methanization. Column conditions: ultra pure nitrogen gas, temperature program: 1 min 423 K, 15 K min^{-1} to 523 K. For quantitative analysis of the gas samples, the chromatograms are compared with those of gas standard samples, containing 1 vol.% CO, CO_2, CH_4, C_2H_2, C_2H_4 and C_2H_6 in N_2 (Scott Specialty Gases).

The liquid samples were obtained by cooling the exit gas in a liquid-nitrogen cooled trap. The liquid samples were diluted (with tetrahydrofuran or *p*-fluorotoluene) and analysed by FID, for this purpose a HP 5890A gas chromatograph equipped with a CP-sil-5-CB (50 m × 0.32 mm i.d.) capillary column and H_2 carrier gas was used. Temperature programs: (1) 5 min 323 K, 5 K min^{-1} to 553 K; (2) 1 min 523 K, 10 K min^{-1} to 553 K. The quantification of the products in the liquid samples ($> C_3$) was performed with help of internal and/or external standards (bromobenzene, dichlorobenzene). Molecular responses of compounds were determined from mixtures of known composition. Products ($> C_3$) were identified by using a HP 5890 GC equipped with a mass spectrometric detector (HP 5970 MSD), using a similar capillary column and He as a carrier gas.

On-line experiments. The set-up consisted of a heated reactor and an analytical facility which enabled the automatic monitoring of thermal decomposition experiments over a programmed temperature range. Constant reaction conditions combined with on-line monitoring and multiple analyses, make it possible to gather very accurate data for kinetic purposes. Gases were introduced by mass flow controllers. The carrier gas nitrogen was led through an externally heated evaporation vessel filled with the liquid substrate to ensure a constant substrate flow. All lines were heated with heating tape to prevent condensation. In the case of the thermolysis of **1** propene was also supplied. The apparatus consists of a quartz tubular flow reactor with an effective volume of 6.25 cm^3 in an electrically heated oven, controlled by a temperature regulator (Fig. 6). The temperature regulator was programmed according to a reaction cycle in which during the first 8 h, every hour, at a specific reaction temperature, a gas sample was injected onto the capillary and onto the packed column. After that a blank run was performed at 523 K, duration 4 h, samples were taken every hour. Therefore, data at reaction conditions are the average of eight measurements, and input data at 523 K are the average of four values, and checked twice a day. GC analyses for the on-line set-up were performed on a Chrompack 438 gas chromatograph. Hydrocarbons were determined by FID on a CP-sil-5-CB (50 m x 0.32 mm i.d.) capillary column. Temperature programs used: 8 min 323 K, 8 K min^{-1} to 433 K then 15 K min^{-1} to 553 K. Gaseous samples (0.5 cm^3 at 523 K) were injected at a split ratio 1:50. The C_1 and C_2 products, including CO and CO_2 were determined on a carbosphere column. The acquisition and editing of the chromatograph data have been executed with the help of a personal computer and special software (mosaïc).

2,3-*Dihydro*-1,4-*benzodioxin. Experimental Conditions.—Off-line.* Residence times in all experiments were between 5 and 6 s (total flow *ca.* 325 mmol h^{-1}) and reaction temperatures between 798 and 873 K. Several diluents were used: benzene, toluene and methanol. The liquid with a 20 mol% concentration of **1** was evaporated by means of the carrier gas stream of

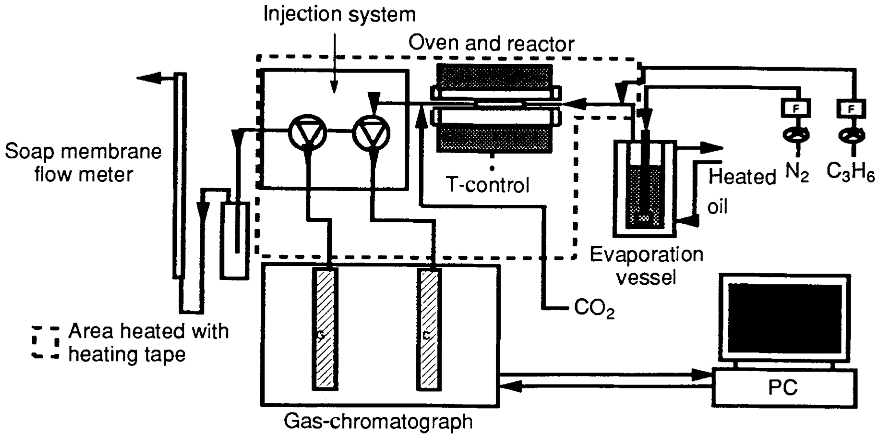


Fig. 6 On-line apparatus

helium. Some experiments were carried out at lower and higher substrate concentrations. Tetrahydrofuran was used to wash out the cold trap vessel to collect all products formed in a certain time. Other solvents did not give homogeneous reaction mixtures. Propene : **1** molar intake ratios were varied between 0 and 100.

On-line. The substrate was evaporated (0.1 mmol h^{-1}) using a nitrogen stream of 12 mmol h^{-1}. Propene was added in excess (82 mmol h^{-1}). The furnace temperature program used consisted of 20 reaction temperatures between 773 and 903 K and blank runs (523 K). A few experiments have been carried out without substrate to monitor the products formed from propene. Carbon dioxide and propene were used as standards to quantify the products.

1,2- *and* 1,4-*Dimethoxybenzene. Experimental Conditions.*—*Off-line.* The substrate and an internal standard (*o*-dichlorobenzene) were diluted in *p*-fluorotoluene. After evaporation they were carried into the reactor by the inert gas stream of helium.

On-line. (Only 1,2-dimethoxybenzene.) Six reaction temperatures between 750 and 830 K were studied at residence times of 4 s. Quantification of products was performed relative to a fixed amount of CO_2, which was added to the gas stream after the reactor.

Chemicals.—1,2- and 1,4-Dimethoxybenzene, >99.5%; *p*-fluorotoluene, >99% Merck-schuchardt; *o*-chlorobenzene, >99%, Merck-schuchardt; 2,3-dihydro-1,4-benzodioxin, Janssen, 99.9%; benzene, Merck-schuchardt, >99%; bromobenzene, >99%, Merck-schuchardt; C_3H_6 and N_2, Air products, >99%; He, Hoekloos.

2-*Methyl*-1,3-*benzodioxole* **7**.—Catechol (48.4 g) and toluene-*p*-sulfonic acid (11.6 mg) in benzene (220 cm^3) were heated under reflux and paraldehyde (115 cm^3) was added in 10 cm^3 aliquots over a period of 6 days. After removal of solvent using a rotary evaporator the reaction mixture was diluted with light petroleum, and catechol, which crystallized, was subsequently removed by filtration. The filtrate was passed through a column of alumina. Removal of solvent yielded 1.5 g of solid material containing **7** (86%) and an impurity ($C_{10}H_{12}O_3$, probably a seven-membered ring compound).

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