

Thermal Hydrogenolysis of Dibenzo-*p*-dioxin and DibenzofuranMariusz K. Cieplik,<sup>[a]</sup> Onno J. Epema,<sup>[b]</sup> and Robert Louw\*<sup>[a]</sup>**Keywords:** Dibenzo-*p*-dioxin / Oxygen heterocycles / Hydrogenation / Kinetics / Reaction mechanisms

The behaviour of dibenzo-*p*-dioxin (DD) and dibenzofuran (DF) was studied in flow reactors in an excess of hydrogen, at atmospheric or elevated pressure (up to 35 bar), in the temperature range 890–1262 K. The experiments at atmospheric pressure were performed with DF or DD as such, while at increased pressures the compounds were introduced as an admixture with benzene. DD gave CO, but also DF as an important product. The rates clearly depended on the hydrogen concentration, and were about an order of magnitude higher than that of the hydrodechlorination of chlorobenzene. The reaction apparently started with the fission of a C–O bond, induced by H atom attack. DF reacted much more slowly, to give CO and hydrocarbons, especially naphthalene

and benzene. Its rate was insensitive to the concentration of H<sub>2</sub>, and the degradation has been interpreted as thermolysis, through C–O bond homolysis, isomerisation and fragmentation, primarily to naphthalene, and C<sub>2</sub>O as the intermediate to CO. The apparent resistance of DF to hydrogenolysis can be understood from its relatively favourable thermodynamic stability. The consequences for the behaviour of polychlorinated DDs and DFs under similar conditions — relevant for the possible application of thermal hydrogenolysis as a waste management technology — are also discussed briefly.

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## Introduction

Benzene, under a pressure of 20–30 bar of hydrogen, reacts smoothly at around 1200 K (927 °C), in seconds, to afford high yields of methane.<sup>[1]</sup> This process appears to proceed through (reversible) H atom addition and isomerisation, hydrogenation to C<sub>6</sub>H<sub>8</sub> species and subsequent splitting into ·CH<sub>3</sub> and ·C<sub>5</sub>H<sub>5</sub> (e.g. cyclopentadienyl) radicals.<sup>[1]</sup> Naphthalene reacts about 10 times more rapidly; this is understood — also on a thermokinetic basis — in terms of an overall easier ring-opening hydrogenolysis.<sup>[2]</sup> The fact that anthracene reacts only marginally more rapidly than naphthalene is explained by the extra energy barrier required for splitting of its central ring, leaving degradation of a side ring as the only effective reaction pathway.<sup>[2]</sup>

Activated carbon, “the ultimate PAH” (PAH = polycyclic aromatic hydrocarbon), is considerably more resistant; its lifetime for gasification to methane is over an hour at 1250 K (970 °C). This highly condensed structure is less open to reaction with H/H<sub>2</sub>, and therefore the effective

breakdown of aromatic rings is slow. Nevertheless, even quite complex PAHs are smoothly degraded in the vapour phase, ultimately to methane, which offers potential for this “dry” gasification as a waste management technology. Halogens can be tolerated even at high concentrations, as these — and other — substituents are displaced by H at a much faster rate than that at which arene rings are degraded.<sup>[1,3,4]</sup> Under these reductive conditions, organic chlorine derivatives exclusively become HCl — unlike in the case of combustion, which also gives free chlorine. Furthermore, “dioxins” (polychlorinated dibenzodioxins and -furans, PCDD/Fs) cannot arise, and, if present, will be detoxified, at least by their hydro-dechlorination to the parent compounds DD and DF.

DD, and certainly DF, can be looked upon as heterocyclic PAH analogues, and so it is of basic interest, both from a scientific viewpoint and to obtain a better insight into the fate of PCDD/Fs when present in waste streams, to determine rates and pathways of conversion of DD and DF and to compare their behaviour with that of, for example, benzene or naphthalene.

## Results

Dibenzo-*p*-dioxin (DD)

The conversion of DD was first investigated at ca. 1 bar, in set-up A (see Exp. Sect.) between 960 and 1153 K, with residence times  $\tau$  in the quartz flow reactor of 2.2–2.6 s. The DD level in the bath gas (H<sub>2</sub> + N<sub>2</sub>) was around 10<sup>−4</sup>

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(mixing ratio). Three representative examples (I–III) are outlined in Table 1. Remarkably, next to CO and ethene as rather prominent degradation products, dibenzofuran (DF) appears as an important product as well — with selectivities of around 50% — together with smaller proportions of benzene, naphthalene and hydroxy-DF.

Table 1. Hydrogenolysis of dibenzo-*p*-dioxin at atmospheric pressure (n.d. = not detected, detection limit ca. 0.03  $\mu\text{mol/h}$ )

| Exp. No. <sup>[a]</sup>          | I              | II   | III  | IV   | V    | VI   |
|----------------------------------|----------------|------|------|------|------|------|
| Temperature [K]                  | 1053           | 1083 | 1133 | 953  | 983  | 1033 |
| Res. time [s]                    | 2.4            | 2.3  | 2.2  | 4.6  | 4.4  | 4.2  |
| Intake [ $\mu\text{mol/h}$ ]     |                |      |      |      |      |      |
| DD                               | 13.0           | 6.54 | 9.72 | 7.53 | 6.22 | 6.87 |
| Trioxane                         | —              | —    | —    | 241  | 207  | 239  |
| Output [ $\mu\text{mol/h}$ ]     |                |      |      |      |      |      |
| Benzene                          | 0.39           | 0.62 | 1.08 | n.d. | n.d. | n.d. |
| Naphthalene                      | 0.13           | 0.29 | 0.88 | n.d. | n.d. | 0.10 |
| DF                               | 1.05           | 1.67 | 4.42 | 0.36 | 0.49 | 1.27 |
| DD                               | 7.07           | 3.30 | 0.33 | 4.25 | 2.62 | 1.63 |
| 2-Hydroxydiphenyl ether          | $\approx 0.03$ | n.d. | n.d. | n.d. | n.d. | n.d. |
| 4-Hydroxydibenzofuran            | 0.98           | 1.21 | 0.49 | 0.62 | 0.72 | 1.01 |
| CO                               | 1.90           | 3.01 | 7.23 | 481  | 514  | 687  |
| C <sub>2</sub> H <sub>4</sub>    | 2.13           | 2.32 | 2.58 | 98.2 | 42.5 | 19.6 |
| C <sub>2</sub> H <sub>6</sub>    | 0.10           | 0.13 | 0.33 | n.d. | n.d. | n.d. |
| DD conversion [%] <sup>[b]</sup> | 45             | 49   | 97   | 44   | 58   | 77   |

<sup>[a]</sup> Pressure: 1.4 bar; total inflow 146 mmol/h; H<sub>2</sub>/N<sub>2</sub> = 3.5 (exp. I–III); 2.4 (exp. IV–VI). <sup>[b]</sup> Other data on DD conversion: 1032 K  $\approx$  20%; 993 K < 5% (in absence of trioxane); 1073 K  $\approx$  90%, 1113 K > 97% (with trioxane).

Next, competitive runs of DD with chlorobenzene (PhCl) were conducted, with the aim of determining relative rates. In the temperature range 950–1090 K, with  $\tau = 4.2$ –4.6 s, a PhCl inflow level of ca.  $10^{-3}$  mol/mol of (H<sub>2</sub> + N<sub>2</sub>) and DD/PhCl ratios of around 0.04, the rates of disappearance of DD were similar, and about a factor of 10 higher than those of PhCl. The degree of conversion of PhCl was only about 20% at the highest temperature. This implies a rate that is a factor of 10 lower than that observed previously, when much higher arene/H<sub>2</sub> intake ratios (e.g., 1:5) were used.<sup>[5]</sup> The reaction of PhCl involves removal of Cl by a hydrogen atom.<sup>[5]</sup> The “spontaneous” splitting of H<sub>2</sub> is very slow, which means that radical-molecule reactions must be sufficiently abundant to establish (near) equilibrium concentrations of  $\cdot\text{H}$ .<sup>[6]</sup> The very low levels ( $10^{-3}$  or less) of aromatics applied in the experiments discussed here may therefore have been insufficient for this.

In order to get around that problem, the effect of addition of sym-trioxane was studied. This cyclic trimer of formaldehyde decomposes above 400 °C into formaldehyde, a known source of H atoms,<sup>[7]</sup> without making the chemistry of interest too complex. Repetition of the DD/PhCl competition experiment with added trioxane (ca. 2 mol per mol of PhCl) indeed produced considerably higher rates, for both compounds. From a series of reactions conducted between 890 and 1090 K (see ref.<sup>[8]</sup> for details) with  $\tau \approx 6$  s, it was inferred that PhCl reached the 50% conversion level at ca. 1050 K, while DD had already done so at 970 K. DF

was again an important product, with selectivities of as much as 60–70% at  $T = 1030$ –1050 K.<sup>[8]</sup> The rate-enhancing effect of formaldehyde was also verified for DD alone, as illustrated by examples IV–VI (Table 1) involving ca. 0.6 mol-% CH<sub>2</sub>O relative to H<sub>2</sub>. Roughly speaking, the same rates as in series I–III were obtained, but at temperatures about 100 degrees lower (see also Figure 1).

### Dibenzofuran (DF)

The reactivity of DF was determined analogously. With ca. 0.1% DF in H<sub>2</sub> and  $\tau \approx 4.0$ –4.2 s, degrees of conversion ranged from <10 to 64% between 1133 and 1213 K, the 50% level of reaction being reached at ca. 1195 K. Clearly DF was reacting much more slowly than DD, which would have already been nearly completely converted at the onset temperature for DF (see Figure 1). Naphthalene and CO were rather prominent products, together with benzene, indene, and lighter hydrocarbons (Table 2). The selectivity to CO was essentially 100%, and the carbon was also quantitatively accounted for ( $100 \pm 2\%$ ).

A separate series in which the H<sub>2</sub> concentration was varied by admixing with nitrogen had no perceptible effect on the rates.

When plotted as a first-order reaction, the rate constant  $k$  for the disappearance of DF obeyed  $\log k/\text{s}^{-1} \approx 13.3 - 76.7 \text{ kcal/mol}/2.3RT$ .<sup>[8]</sup> This was suggestive of a “spontaneous” pyrolytic conversion rather than a reaction induced by hydrogen, and in this light we thought it worthwhile to consider the hydrogenolysis of DF at elevated H<sub>2</sub> pressures, also comparing its reactivity with those of aromatic hydrocarbons.<sup>[1,2]</sup>

This was done by admixing DF with several PAHs dissolved in an excess of benzene (Table 3). With residence times of  $21 \pm 2$  seconds, pressures of ca. 35 bar and a molar H<sub>2</sub>/benzene inflow ratio of 33, runs were conducted in set-up B (section 5.2). Data for experiments at temperatures between 1157 and 1262 K are shown in Table 3. At the highest  $T$ , conversion of both PAH and DF was essentially complete — with a recovery of benzene of ca. 7% — again with a quantitative yield of CO from DF.

Outputs of CO as a percentage of the inflow of DF are plotted in Figure 1. As a measure of the levels of conversion of the hydrocarbons, the output of methane (plus the small amounts of C<sub>2</sub> hydrocarbons) as a percentage of the total carbon in the feed is also depicted.

It can be seen that the degree of conversion of DF at 1170 K is ca. 30%, seemingly the same value as for with ca. 1 bar of H<sub>2</sub>. While it should be noted that the residence times were ca. five times longer — and that data from greatly different set-ups were being compared — there was no sign of a higher rate with increased H<sub>2</sub> concentration. The 35 bar result can also be compared with that previously reported for naphthalene (N) — 30% conversion at 1133 K (860 °C)<sup>[2]</sup> at approximately the same pressure and reaction time — meaning that DF reacts considerably more slowly than N under the given conditions.

After we had concluded our work, Winkler et al. presented rate and product data on the *pyrolysis* of DF in a

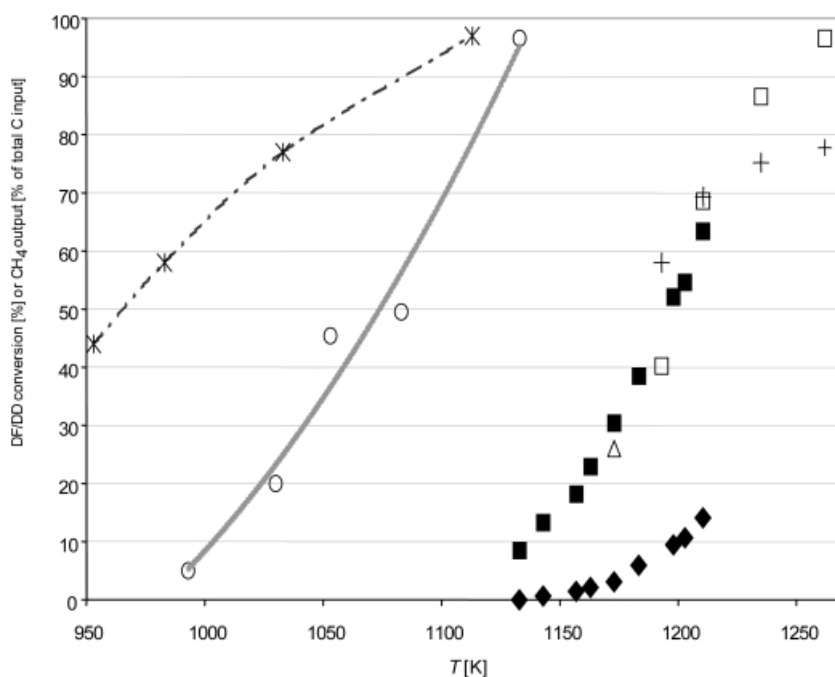


Figure 1. Overview of DD/DF conversions; x: DD conversion (with trioxane, 1.4 bar, 4.2–4.6 s); O: DD conversion (1.4 bar 2.2–2.4 s); ■ DF conversion (1.1 bar, 4.0–4.2 s), based on DF recovery; □ DF conversion (35 bar, 20 s), based on CO output; Δ DF conversion;<sup>[9]</sup> ◆ CH<sub>4</sub> output (1.4 bar, 4 s), + CH<sub>4</sub> output (35 bar, 20 s)

Table 2. Hydrogenolysis of DF

| Temperature <sup>[a]</sup><br>[K] | 1133  | 1143 | 1153 | 1163 | 1173 | 1183 | 1193 | 1203 | 1213 |
|-----------------------------------|-------|------|------|------|------|------|------|------|------|
| Intake [μmol/h]                   |       |      |      |      |      |      |      |      |      |
| DF                                | 14.5  | 14.5 | 14.2 | 14.1 | 14.0 | 13.8 | 13.7 | 13.6 | 13.6 |
| Output [μmol/h]                   |       |      |      |      |      |      |      |      |      |
| CO                                | 0.60  | 1.65 | 2.04 | 3.12 | 3.87 | 5.44 | 7.07 | 7.42 | 8.94 |
| CH <sub>4</sub>                   | 0.79  | 1.91 | 2.45 | 4.42 | 5.92 | 10.4 | 15.6 | 17.8 | 23.5 |
| C <sub>2</sub> H <sub>2</sub>     | 0.29  | 0.59 | 0.66 | 0.72 | 0.66 | 0.64 | 0.78 | 0.70 | 0.74 |
| C <sub>2</sub> H <sub>4</sub>     | 0.21  | 0.81 | 1.05 | 1.64 | 2.04 | 3.06 | 4.14 | 4.09 | 4.60 |
| C <sub>2</sub> H <sub>6</sub>     | 0.17  | 0.15 | 0.28 | 0.51 | 0.56 | 0.90 | 1.12 | 1.05 | 1.20 |
| Cyclopentadiene                   | 0.19  | 0.27 | 0.34 | 0.38 | 0.38 | 0.36 | 0.35 | 0.32 | 0.27 |
| Benzene                           | 0.73  | 0.81 | 1.06 | 1.53 | 2.07 | 2.57 | 3.02 | 3.72 | 2.70 |
| Toluene                           | n.d.  | 0.03 | 0.03 | 0.03 | 0.04 | 0.04 | 0.07 | 0.07 | 0.07 |
| Indene                            | 0.27  | 0.31 | 0.44 | 0.60 | 0.82 | 0.97 | 1.05 | 1.18 | 1.24 |
| Naphthalene                       | 0.51  | 0.62 | 0.78 | 0.98 | 1.42 | 1.76 | 2.04 | 2.38 | 2.77 |
| Biphenyl                          | 0.05  | 0.05 | 0.05 | 0.04 | 0.04 | 0.03 | 0.04 | 0.03 | 0.03 |
| Biphenylene                       | 0.03  | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | n.d. | n.d. | n.d. |
| DF                                | 13.0  | 12.5 | 11.8 | 10.9 | 9.7  | 8.5  | 7.1  | 6.2  | 5.0  |
| DF conversion [%]                 | (8.5) | ≈13  | 17   | 23   | 30   | 38.5 | 48   | 54.5 | 63.5 |

<sup>[a]</sup> At 1.1 bar; carrier gas: H<sub>2</sub> only, 60 mmol/h, residence time  $\tau \approx 4.2$  s (1133 K) to 4.0 s (1213 K).

large excess of argon (1 bar, 1173 K) with residence times of ca. 20 s.<sup>[9]</sup> The pyrolysate contained 74% of DF, and N was the most prominent product. Rate data were not reported explicitly, but for complete materials balance the degree of conversion should have been 26%; for less complete recoveries the conversion would have been accordingly higher. The data point for the “minimum” value has been included in Figure 1.

Table 3. High-pressure hydrogenolysis of dibenzofuran/hydrocarbon mixtures

| Temperature <sup>[a]</sup><br>[K]         | 1157  | 1198  | 1214  | 1262  |
|-------------------------------------------|-------|-------|-------|-------|
| Intake [mmol/h]                           |       |       |       |       |
| Benzene                                   | 14.8  | 16.2  | 14.9  | 15.0  |
| Indene                                    | 0.25  | 0.26  | 0.24  | 0.24  |
| Naphthalene                               | 1.11  | 1.10  | 1.03  | 1.07  |
| Biphenyl                                  | 0.16  | 0.16  | 0.15  | 0.16  |
| Phenanthrene                              | 0.12  | 0.12  | 0.11  | 0.12  |
| DF                                        | 0.29  | 0.28  | 0.27  | 0.29  |
| Output [mmol/h]                           |       |       |       |       |
| CO                                        | 0.07  | 0.13  | 0.19  | 0.28  |
| CH <sub>4</sub>                           | 48.92 | 71.83 | 78.37 | 86.26 |
| C <sub>2</sub> H <sub>6</sub>             | 1.44  | 0.55  | 0.40  | 0.101 |
| Benzene                                   | 7.05  | 5.80  | 3.25  | 0.91  |
| Toluene                                   | 0.01  | <0.01 | <0.01 | <0.01 |
| Indene                                    | <0.01 | <0.01 | <0.01 | n.d.  |
| Naphthalene                               | 0.05  | 0.04  | 0.05  | <0.01 |
| Biphenyl                                  | 0.04  | 0.03  | 0.05  | <0.01 |
| Phenanthrene                              | <0.01 | 0.01  | <0.01 | n.d.  |
| DF conversion <sup>[b]</sup> [%]          | 24    | 46.5  | 70    | 96.5  |
| CH <sub>4</sub> [% of total carbon input] | 44.7  | 61.2  | 71.2  | 77.8  |

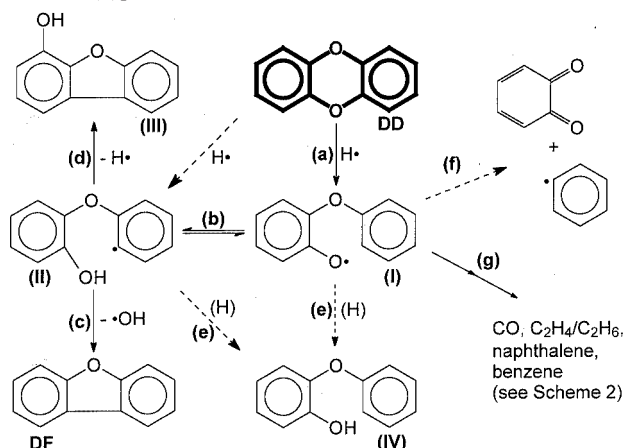
<sup>[a]</sup> 35 bar of H<sub>2</sub>,  $\tau \approx 21$  s, H<sub>2</sub>/benzene molar intake ratio ca. 33. <sup>[b]</sup> Based on CO output.

Keeping in mind that the studies were performed in different laboratories and with different set-ups, it is still striking that the rate of decomposition of DF under 1 bar of argon apparently differs little from that under 35 bar of hydrogen.

## Discussion

### Dibenzo-*p*-dioxin

As the rate of thermal hydrogenolysis clearly depends on the concentration of (atomic) hydrogen, the first step in the conversion of DD would appear to be the reaction between  $H^\bullet$  and a C–O bond. Upon *ipso*-addition to C and subsequent breaking of the relatively weak C–O bond, the substituted phenoxyl radical I would be formed [Scheme 1, reaction (a)].



Scheme 1

The key intermediate I could isomerize to species II by intramolecular H abstraction [step (b)]; it could also arise by direct attack of  $H^\bullet$  on oxygen in DD. The conversion  $I \rightarrow II$  is endothermic (by ca. 27 kcal/mol<sup>[10]</sup>), and therefore reversible and very probably equilibrated. Radical II is the logical precursor of both DF — by loss of  $\cdot OH$  [reaction (c)] — and of its 4-hydroxy derivative III, formed by ring-closure with loss of  $\cdot H$  [reaction (d)]. Intermolecular hydrogenation of I and/or II [reaction (e)] would appear to be of

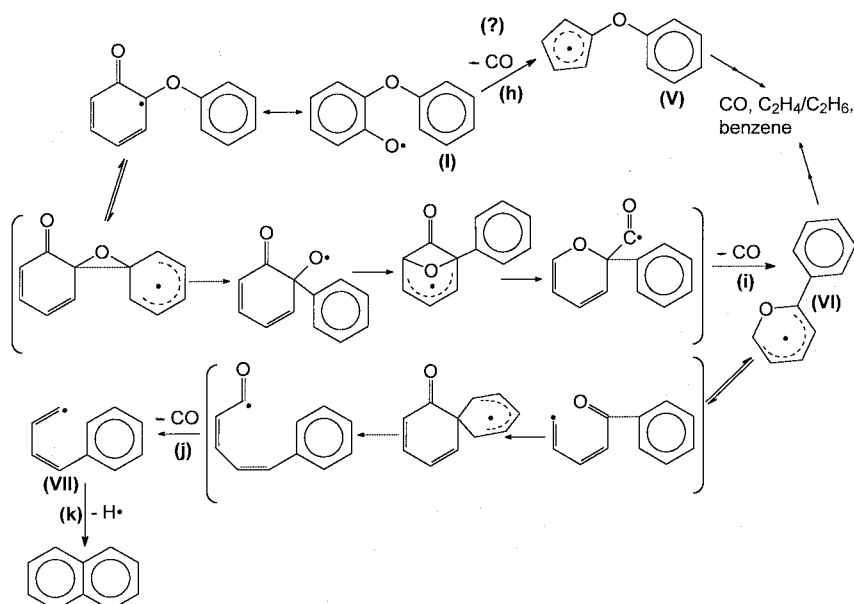
minor importance, as IV was only found at trace levels at “lower” temperatures. (At higher  $T$ , compound IV would also be rapidly hydrogenolysed, either via radical I or not).

Splitting of I into *o*-quinone and phenyl [reaction (f)] to explain the formation of benzene, CO and  $C_2$  hydrocarbons is attractive, but the activation energy would probably be too high to compete successfully with steps b–d.<sup>[13]</sup> Instead, radical I could provide a route to these degradation products — as well as naphthalene — after rearrangement [pathway (g)], as further illustrated in Scheme 2.

By analogy with the parent phenoxyl radical,<sup>[14]</sup> I would be a candidate to split off CO directly to give radical V [reaction (h)] but for thermochemical-kinetic reasons this would not be likely to be important. Rather, a rearrangement culminating in loss of CO, by, for example, pathway (i), producing radical VI, seems straightforward. Both V and VI could be degraded to benzene etc., but further rearrangement could result in loss of another CO molecule, as in pathway (j), with radical VII as a precursor of naphthalene.

Naphthalene may also be formed by condensation of two cyclopentadienyl radicals,<sup>[15]</sup> should these act as intermediates. Substituted analogues such as V can react accordingly, with loss of (phenoxy) substituents either during the process or after the naphthalene structure has been established.

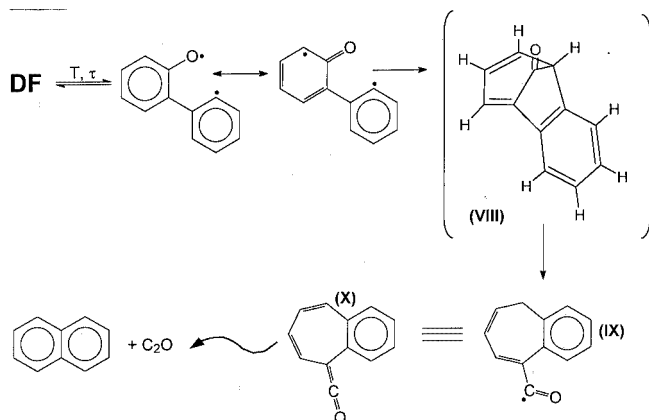
The first step in the conversion of DD with  $H^\bullet$  [reaction (a), Scheme 1] should be irreversible, because conversion of I to DF and III via radical II would be easier, in view of the lower energy barriers.<sup>[10]</sup> That DD reacts considerably more rapidly than chlorobenzene is primarily due to the statistical factor of 4; the *per site* reactivity may also differ somewhat, although in general, rates for — straightforward — displacements from monosubstituted benzenes  $PhZ + \cdot H \rightarrow PhH$  vary little with Z.<sup>[3]</sup>



Scheme 2

## Dibenzofuran

As reported above, the reaction rates of dibenzofuran do not appear to depend on the hydrogen concentration/pressure. Moreover, Winkler et al.<sup>[9]</sup> have recently found that pyrolysis of DF gave not only similar rates, but also similar main products: carbon monoxide and naphthalene. All this strongly points to a unimolecular reaction. Scheme 3 presents an interpretation, based on the overall stoichiometry  $\text{DF} \rightarrow \text{naphthalene} + \text{C}_2\text{O}$ .



Scheme 3

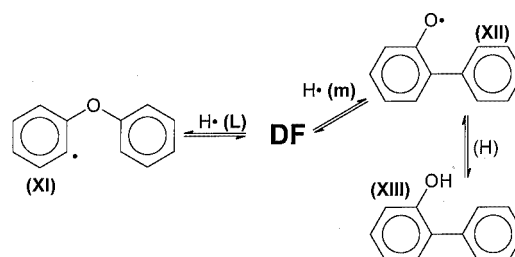
Upon C–O bond cleavage, DF could isomerise to species VIII (5H-5,9-methanobenzo[7]annulen-10-one<sup>[16]</sup>) and, through radical IX, ultimately to compound X (5H-benzo[7]annulen-5-ylidenemethanone<sup>[16]</sup>). This could split off  $\text{C}_2\text{O}$ , by analogy with cheletropic decarbonylation.<sup>[17]</sup> Dicarboxyl monoxide is known to decompose even at relatively mild temperatures,<sup>[18]</sup> yielding atomic carbon and CO.

The thermochemical-kinetic details of this mechanism are not discussed here, one reason being that the published heats of formation both of DF (from 11 to 20 kcal/mol<sup>[19]</sup>)

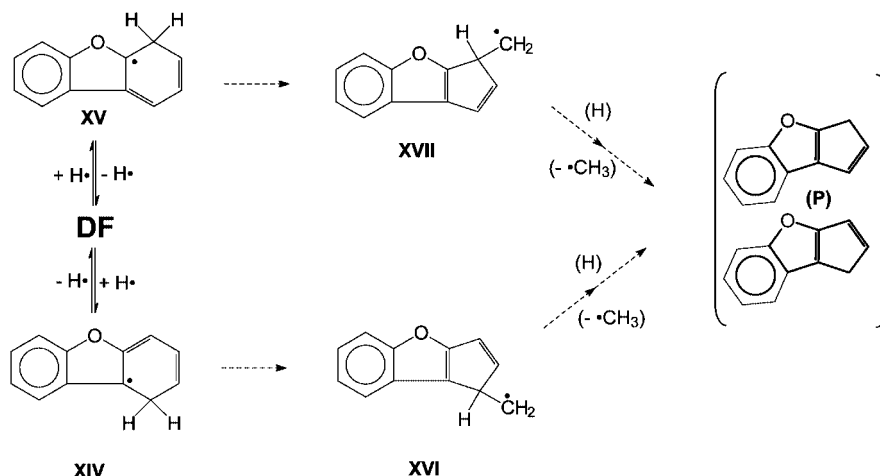
and of  $\text{C}_2\text{O}$  (from 58<sup>[11]</sup> to 68.5<sup>[18]</sup> kcal/mol) differ widely. If values of 11 and 58 kcal/mol, respectively, were taken, the overall (standard) heat of reaction of DF to  $\text{C}_2\text{O}$  and naphthalene ( $\Delta_r H^\circ = 36$  kcal/mol) would be 74 kcal/mol, in fair agreement with the observed Arrhenius activation energy of 77 kcal/mol.

Interestingly, benzofuran derivatives could not be detected. This could mean two things: either that, if formed, they were rapidly converted, or that no such species were formed. This would be consonant with the fact that hydrogenolysis of DF is insignificant compared with its direct thermolysis. To understand why DF — which at first sight is a regular (di)substituted benzene — resists hydrogenolytic splitting, consider Schemes 4 and 5.

Scheme 4 depicts the opening of the central ring by  $\text{H}^\bullet$  to give radicals XI and XII. No doubt the forward reaction (L) should occur easily, by analogy with the splitting of biphenyl,<sup>[20]</sup> but there is no other fate than to revert to DF and  $\text{H}^\bullet$ , a step that is even mildly exothermic. Similarly, the formation of XII [reaction (m)] should be easy. Although reversal of XII to DF and  $\text{H}^\bullet$  should — on the basis of current thermochemistry — be endothermic by some 30 kcal/mol, it still appears to be fast at the high temperature involved, compared with possible “exits” through bimo-



Scheme 4



Scheme 5

lecular reactions, such as formation of *o*-hydroxybiphenyl XIII and its hydrogenolysis.

Scheme 5 shows the addition of H<sup>•</sup> to positions 1 and 4 in DF, resulting in radicals XIV and XV (additions to the other two unsubstituted positions 2 and 3 are not depicted, because the behaviour of the resulting radicals would be analogous to that of XIV and XV).

If XIV and XV were to react analogously with benzene,<sup>[1]</sup> (reversible) isomerisation to XVI/XVII would occur. Further hydrogenolysis (with loss of one carbon as 'CH<sub>3</sub>'<sup>[1]</sup>) would give rise to cyclopentadiene derivatives (P). These are analogues of dihydropentalene, known to be highly strained.<sup>[21]</sup> This "handicap" is already present in species XVI and XVII, so altogether even their formation is heavily disfavoured compared with the base case benzene.

### Relative Rates

In our earlier papers,<sup>[1,2]</sup> the relative rates for the conversions of benzene (B), naphthalene (N), and chlorobenzene, modelled for 1250 K and 25 bar H<sub>2</sub>, were shown to be B/PhCl = 0.1:1:35.

To put DD on this scale, the result (faster than PhCl by a factor of 10 at ca. 1000 K) has to be translated to 1250 K, and a value of ca. 8 would be expected.<sup>[22]</sup> Obviously, DF reacted very much more slowly than DD: Figure 1 shows that the *T*<sub>50%</sub> values for DD and DF are some 230 °C apart. On this basis, DF has been calculated to react ca. 4 × 10<sup>3</sup> times more slowly than DD (ca. 14 times more slowly than N) under the model conditions used.<sup>[24]</sup> All this implies the following order (Table 4, relative rates compared with N = 1).

Table 4. Relative rates at 1250 K, 25 bar H<sub>2</sub>

| Compound (in order of increasing rates) | DF ≈   | B < | N << | PhCl < | DD                    |
|-----------------------------------------|--------|-----|------|--------|-----------------------|
| Relative rate                           | ≈ 0.07 | 0.1 | 1    | 35     | ≈ 3 · 10 <sup>2</sup> |

On going from 25 to 1 bar of hydrogen (with sufficiently high concentrations of organics to ensure equilibration between H<sub>2</sub> and 'H), the rates for PhCl and DD — and presumably also for B and N — went down (by a factor of 5), with little if any change in their relative rates. While DF is insensitive to H<sub>2</sub> concentration, its relative rate can approach that of N. In any case, the fact remains that hydrodechlorination (of PhCl) and hydrogenolytic conversion of DD are much faster than the degradation (thermolysis) of DF. Polychlorinated DFs will therefore undergo repeated hydrodechlorination (ultimately to DF) rather than being degraded. Likewise, polychlorinated DDs will be subject to hydrodechlorination, but, by analogy with DD itself, formation of chlorinated DFs as intermediate products would be expected to be more important.

### Conclusions

Dibenzo-*p*-dioxin was relatively easily converted under a hydrogen atmosphere at *T* around 1000 K, about 10 times more rapidly than the reaction of chlorobenzene to give benzene and HCl. Interestingly, together with CO, dibenzofuran (DF) was an important product. Both processes were sensitive to the concentration of H atoms, which appeared to react by addition to (Cl- or O-) substituted carbons as a first step.

DF was much more resistant to degradation. Moreover, the rates did not seem to depend on the hydrogen (atom) concentration, as shown by comparison between hydrogenolysis — from 1–35 bar of H<sub>2</sub> — and a recent report on thermolysis in argon. Naphthalene (N) was an important product throughout, and a thermolysis mechanism involving C–O fission and isomerization has been put forward. While the overall rates for the conversion of DF and N were quite comparable, hydrogenolytic ring-opening in DF appeared to be slow. An explanation for this has also been presented.

The results are of interest for possible application of thermal hydrogenolysis in the management of (hazardous) waste. On the basis of the found or calculated relative rates, the expected fate of polychlorinated DDs is that conversion into chlorinated DFs would be a more important pathway than hydrodechlorination; DD and analogues — if present in the starting mixture — would disappear relatively rapidly anyway. The polychlorinated DFs should be smoothly dechlorinated, just like chlorobenzenes etc. (and hence, detoxified) to leave DF — together with other (aromatic) compounds, especially hydrocarbons — as a rather stable compound. With, for example, >99% "mineralisation" of organic chlorine to HCl, this could be a very acceptable result. There is little need to destroy DF for health or safety reasons (or N; some carcinogenic PAHs may have been formed), but, if desired, temperatures above 1300 K should be chosen, so as to gasify thoroughly even benzene and derivatives, if not soot and carbon, to methane,<sup>[1,2]</sup> questions about exact mechanisms, molecular or free-radical, of conversions of DD/DFs then become quite pointless.

### Experimental Section

**Atmospheric Pressure Set-Up (A):** Atmospheric pressure experiments were performed in the set-up shown schematically in Figure 2.<sup>[8]</sup> The effective volume of the reactor is ca. 6 mL. Hydrogen and nitrogen were introduced by means of electronic mass flow controllers (Brooks 5850TR). Methane was used as a reference gas. Liquid and solid reagents were evaporated/melted in an impinger vessel and carried into the reactor system by a calibrated nitrogen flow.

**High Pressure Set-Up (B):** The high pressure set-up and the experimental procedures applied in this study have been described elsewhere.<sup>[1]</sup>

**Sampling and Analyses. Atmospheric Pressure Experiments:** Samples of the effluent gases were taken by means of six-port sam-

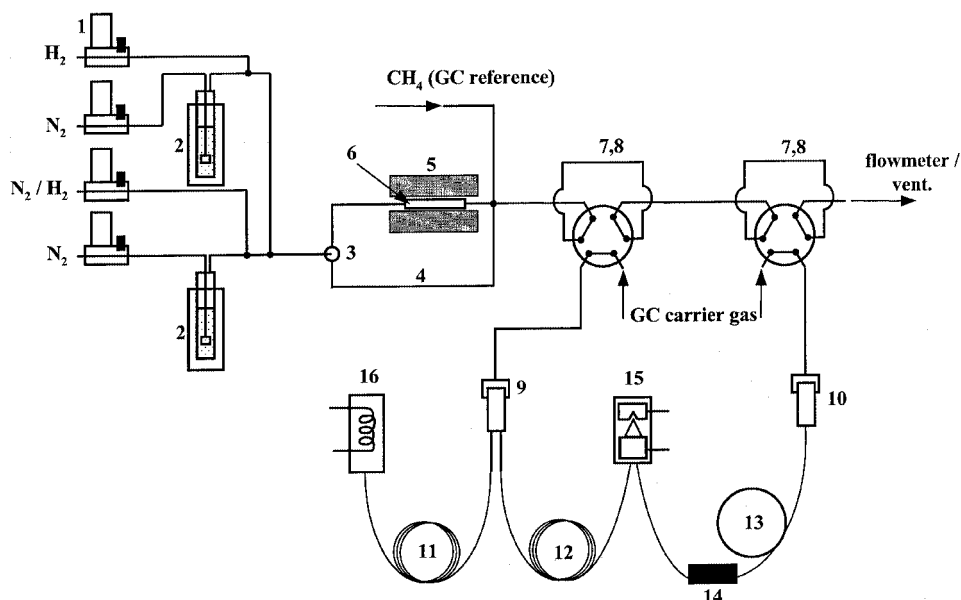


Figure 2. Experimental setup A: 1. mass flow controllers; 2. evaporation vessels; 3. valve; 4. bypass; 5. oven; 6. reactor; 7. sample valve; 8. sample loops; 9. split/splitless capillary injection port; 10. splitless packed injection port; 11. capillary column (mol. sieves 5 Å); 12. capillary column (CP-SIL 5); 13. packed column (Carbosphere); 14. methanizer; 15. FID; 16. TCD

pling valves (Valco C6WT-HC) mounted in a HP 5890 series II Gas Chromatograph, equipped with three columns: a packed one connected to a FID methaniser (CO, CO<sub>2</sub> and C<sub>1</sub>/C<sub>3</sub> hydrocarbons analyses); a capillary Chrompack CP-Sil5 (50 m, 0.32 mm ID) column connected to a FID (C<sub>5</sub>–C<sub>18</sub> hydrocarbons) and a 5 Å mol. sieves column connected to a TCD.

Unknown products were identified by off-line GC/MS analysis on a HP 5970/HP 5890 instrument.

**High-Pressure Experiments:** For each run, two liquid (organic) fractions were collected: one in the pressurised trap of the reactor system and one in a cold trap. Samples were analysed by GC/FID (HP5890 quantification) and GC/MS (HP5890/HP5972 scan mode, MM range 30–350; with a standard NIST NBS75 spectrum library – qualitative analysis). Standard method: init. temp. 50 °C; init. time 5 min; rise 10 °C/min; final temp. 280 °C, final time 10 min; column: Chrompack CP-SIL 5 CB, 50 m × 0.32 mm × 0.4 µm; carrier gas: H<sub>2</sub> (GC/FID), He (GC/MS); column head pressure 90 kPa. Monobromobenzene was applied as a co-injection standard (ca. 0.1 g per sample).

During each run, eight to twelve 0.5 mL gaseous samples were taken from the sampling point at the end of the system. Analyses of C<sub>1</sub>/C<sub>2</sub> compounds were carried out on a Packard 428 gas chromatograph equipped with a packed column (Alltech, Carbosphere, 86–100 MESH), a FID detector and a methaniser. Peak areas were compared to those of a standard mixture of CO, CO<sub>2</sub>, methane, acetylene, ethylene, and ethane, each 1% (v/v) in nitrogen.

To take the collecting time into account, results are expressed in time-dependent units (mmol/h).

**Chemicals:** The following chemicals were utilised: benzene [Merck p.a., 99% (distilled)], dibenzo-*p*-dioxin (synthesised, method described by Dittus et al. in ref.<sup>[25]</sup>), dibenzofuran (Fluka, >99%), monobromobenzene (Baker, >99.5%), naphthalene (Janssen Chimica, >99%), *n*-pentane (Baker Analysed, >99%), hydrogen (Air

Products, 99.995%), methane (Air Products, 99.995%), nitrogen (Air Products 99.995%).

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