Gas-Phase Hydrogenolysis of Benzene and Derivatives at Elevated Pressure; Methane Formation

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Keywords: Benzene / Chlorobenzene / Gasification / Hydrogenolysis / Toluene

Benzene, in 20–30 bar of hydrogen, reacts smoothly in a quartz tubular flow reactor between 1163–1262 K, to give high yields of methane. With dwell times of 3–23 s, degrees of conversion ranged from 10 to 95%. Substituents such as Cl and CH_3 are displaced more easily: ca. 350 times more rapidly at 1250 K. Mechanisms are discussed on a quantitative thermochemical-kinetic basis. Of the alternatives considered, only a pathway through H atom addition, (reversible) isomerisation of $C_6H_7\cdot$ species, H-transfer from H_2 to give – for example – methylcyclopentadiene (**F**), followed by splitting into $\cdot CH_3$ and cyclopentadienyl radical (**G**), would fully explain the observed rates of conversion of benzene.

Introduction

Thermal hydrodehalogenation (THD) has been proposed as a good alternative means for the combustion of halogenated hazardous wastes.[1,2] Organohalogen compounds (OHC) are converted into hydrocarbons (and acids) in an atmosphere of hydrogen at temperatures below 1000 °C, in a few seconds and at normal pressure. In the case of OHCs lacking the possibility for smooth molecular 1,2-HCl elimination − well-known in common chloroalkanes − the dehalogenation reaction involves attack by H atoms as a key step, schematically represented in Equation (1).

$$RX + H\cdot \rightarrow RH + X\cdot \qquad (1)$$

Important examples of such recalcitrant RX moieties include (poly)halogenated methanes,[3] benzenes[4] and biphenyls.[5] Under the reducing conditions used, the formation of chlorinated dioxins is not possible. If PCDDs or PCDFs are present in the feed, they are converted like other aromatic OHCs: at least to nontoxic lower-to-nonchlorinated analogues, and ultimately to hydrocarbons. Some soot can be formed, although much less than under pyrolysis.

Logically, under effective THD conditions, the original structures R of RX do not (fully) survive. Aliphatic OHCs, while becoming alkanes and/or alkenes, are subject to thermal '(hydro)cracking'. Altogether, the chemistry of C−C bond breaking and formation is kinetically controlled. The amounts of methane, though substantial, are still far below levels which would hold at thermodynamic equilibrium.

(Poly)substituted benzenes ultimately yield benzene as a prominent product, meaning that desubstitution [Equation (1)] is a general phenomenon.[6] These conversions are invariably accompanied by formation of small proportions of polycyclic aromatic hydrocarbons (PAHs), together with biphenyl, naphthalene etc. At first sight, benzene may appear a stable compound − at least more stable thermally than methane. However, benzene yields detectable amounts of biphenyl even at 500 °C[7] [Equation (2)].

$$2\,C_6H_6 \rightarrow C_6H_5{-}C_6H_5 + H_2 \qquad (2)$$

$$C_6H_6 + H\cdot \rightleftarrows \cdot C_6H_7 \rightarrow\rightarrow \cdot CH_3 \qquad (3)$$

Under THD-like conditions, (chloro)benzenes also produce methane (and C_2- hydrocarbons) even below 600 °C, with molar yields reaching the percent level at 900 °C.[8] Ring-opening and/or ring-contraction must have been responsible, presumably through cyclohexadienyl radicals ($\cdot C_6H_7$), which can rearrange to 5-membered ring isomers and thence yield methyl radicals [Equation (3)].

In this context, it is worth noting that (labelled) benzenes, when thermolysed (at 1100 °C, 2 s dwell time), display automerisation (such as 1,2-interchange of C-atoms).[9,10] Several potential mechanisms for this phenomenon have been put forward; if it is considered as an intramolecular topomerization, calculations point to various parallel steps, with activation barriers around 95 kcal mol^{-1}.[11] Reactions with added H_2 appear to be faster,[10] and under these conditions radical (chain) steps may prevail.

Under much more drastic conditions (1200−1500 °C, 30−80 bar, in the presence of steam), benzene and derivatives are (completely) gasified.[12] It is quite likely that radical reactions such as H atom attack, isomerisation and/or fragmentation again constitute the first steps of that breakdown.

In order to obtain a better insight into rates, products and mechanism in the hydrogenolysis of benzenes, we have studied the behaviour of benzene, toluene and chlorobenzene in the temperature range of 750−1100 °C and at pressures up to 36 bar, employing a quartz flow reactor system, so as to bridge the gap between the "mild" THD conditions of our earlier studies and those of (full) gasification.

In forthcoming papers, higher analogues of benzene as well as O and N heteroatomic derivatives will be reported on.

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1434−193X/01/0611−2101 $ 17.50+.50/0

Results and Discussion

a) Chlorobenzene

The dehalogenation of chlorinated benzenes at atmospheric pressure has been extensively studied previously.[4,8,13,14] Reactions proceed smoothly around 1050 K and high levels of dechlorination (> 99.95%) are reached in a few seconds at T > 1200 K. The mechanism involves attack by H atoms − present in about the concentration dictated by thermodynamic equilibrium with H_2 − mostly by addition to the C bearing the Cl, with subsequent loss of Cl· (*ipso* substitution) and, to a smaller extent, by chlorine abstraction.[15] This implies a half-order dependence on $[H_2]$ and pseudo-first order behaviour in an excess of hydrogen; the rate constant for chlorobenzene hence obeys log (k/s^{-1}) = 10.9 −57.5 [kcal $mol^{-1}/2.3RT$].[4]

For comparison, and also to calibrate the new set-up, experiments with chlorobenzene were performed at pressures around 25 bar in the temperature range from 1011 to 1183 K. With a molar ratio of H_2:chlorobenzene of 3.0 and dwell times of ca 3.5 s, the conversions to HCl (and, mainly, benzene) ranged from 41% at 1011 K, through ca. 85% at 1077 K, to 99.3% at 1183 K. Using the rate parameters mentioned above, log $k = -1.56$ at 1011 K for 1 bar of hydrogen; effectively in ca 20 bar of H_2 and a square root dependence, log $k = -0.9$, implying a calculated conversion of just over 30% for our pressurised system. Given the differences in set-ups, the observed value of 41% is close enough to accept further measurements as trustworthy. An analogous calculation for 1077 K, assuming plugflow, results in an expected 86% conversion, whereas we found ≈ 85%.

In comparison with experiments at 1 bar, little soot was formed: at 1183 K only 0.35 mass percent of the chlorobenzene. Other products, as expected, were biphenyl and naphthalene; interestingly, a perceptible amount of toluene (ca 0.7% on benzene) was also seen. This reflects the fact that ca. 25% (molar) of methane is produced: some four times as much as in our 1 bar experiment [see ref.[8], exp. M] and in half the dwell time. The effect of using a higher concentration of hydrogen is also seen in the output of C_2 hydrocarbons: at 1 bar, C_2's totalled 24 mol % based on methane, with an ethane/ethene/acetylene ratio of 25:70:5. In the present run at 1183 K, C_2's were only a few percent, based on methane, and the ethane/ethene ratio was 9.3, with negligible acetylene.

b) Toluene

Methane is now a primary desubstitution product and it is already clearly formed under relatively mild conditions. In 25 bar of H_2, in 3 seconds, CH_4 was formed in 0.17% yield at 840 K, increasing to 26% at 982 K. If it is accepted that the rate of displacement is governed by reaction (1), $RX = C_6H_5{-}CH_3$ with [H·] at thermodynamic equilibrium (calculated to be $10^{-10.05}$ M in 25 bar H_2 at 982 K [16]) and with $k = 10^{8.93}$ M^{-1} s^{-1},[15] the calculated degree of conversion in 3 s, assuming plugflow, is 20%. At 1130 K and 26 bar, the methane output is ca 200 mol % based on the toluene feed, showing not only that the methyl group has been split off, but that the benzene ring has also been violated. As well as methane, a little ethane (about 1.5% based on methane in the latter case) was seen. The ethane/methane ratio decreases with increasing temperature and with increasing hydrogen pressure − indicating that much of the chemistry at these high temperatures is based on partial equilibria, such as that between benzene + CH_3· and toluene + H·; furthermore, ethane is also no longer stable and can dissociate into 2 methyl radicals (vide infra).

Under identical circumstances, toluene is desubstituted somewhat more rapidly than chlorobenzene; in one example of a competition experiment, conversions were 87 and 82%, respectively. This is consistent with known rate parameters for the reaction of the two compounds with H atoms.[15]

c) Benzene

Next, the reactivity of benzene in hydrogen (12-fold molar amount) was investigated in the temperature range 1163−1262 K. Representative examples are collected in Table 1. Residence times at the higher temperature were varied by changing (lowering) the inflow rates of benzene and hydrogen.

Table 1. Conversion of benzene to methane

Exp. no.[a]	*T* [K]	Pressure [bar]	Time [s]	[mol % based on benzene]
1	1163	21	2.8	23
2	1207	23.5	3.1	102
3	1229	25	3.2	121
4	1249	10	7.9	91
5	1257	24	3.0	149
6	1248	29	4.1	158
7	1257	31	7.8	224
8	1258	36	23.1	≈ 400
9	1262	34	21.5	≈ 420
N[b]	1173	1	7.5	3.7

[a] Experiments 1−9 molar ratio H_2/benzene = 12. − [b] From ref.[8] ratio H_2/benzene = 6.

At 1163 K, when using hydrogen pressures of 20 bar and above, the degree of formation of methane is already quite substantial; at 1229 K the yield is ca 120 mol % (exp. 3), constituting a benzene conversion of ca. 20% if 6 mol of methane are formed from 1 mol of benzene. This tallies well with the result for toluene at that temperature mentioned above. The methane output is no less than ca 400 mol % in exp. 8.

With essentially no sooting, and with other products at the percent level or less (vide infra), the balance in the product mix should be unconverted benzene. When properly analysed (contents of liquid traps, and accounting for the benzene present in the exit gaseous phase in comparison with blank runs), carbon balances were well over 90%.

As well as methane (and benzene), a little ethane was observed. While it comprised ca 15 mol % based on methane in exp. 1, it was only 2% in exp. 3, 1.1% in exp. 5, 0.7 mol % based on methane in exp. 6, and 0.2% from exp. 8.

As mentioned previously, ethane becomes unstable at these temperatures; using best available rate parameters[17] the calculated half-life for C−C homolysis is still about 1 second at 1163 K, but less than 0.1 s at 1262 K. Ethene is seen at trace levels only; in exp. 5 it is 4.4% based on ethane.

Additional experiments have shown that, at this temperature, the ethane/ethene ratio varies about linearly with the hydrogen pressure, which shows that the process $C_2H_4 + H_2 \rightleftarrows C_2H_6$ is at (pseudo)equilibrium. Acetylene is below detection; if formed in the process it will also be 'gasified', through hydrogenation and hydrogenolysis.

To illustrate the formation/survival of other (semivolatile) products, results from exp. 6 (in which ≈ 50% benzene was recovered), in mol % based on converted benzene, were as follows:

Toluene (tol) (0.8), naphthalene (naph) (1.5), biphenyl (biph) (1.3), indene (ind) (0.05), acenaphthene (ace) (0.09), fluorene (flu) (0.14), pyrene (pyr) (0.15). Likewise, in exp. 8 (with ≈ 90% of benzene converted), outputs of said compounds were tol:(0.6), naph:(0.5), biph:(0.8), ind:(0.04), ace:(0.04) flu:(0.08) and pyr:(0.24), respectively.

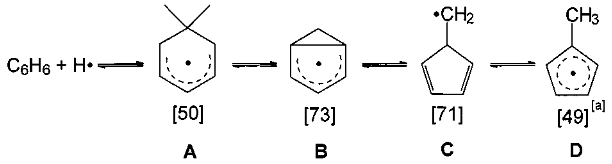
d) Rates

It is obvious that benzene smoothly gives methane under these conditions, with degrees of conversion ranging from a few percent to well over 90%. While the formation of other products is briefly commented on later, the focus is on the question of which key step(s) is (are) responsible for the 'methanisation' of benzene. One way or another, the six-membered ring will be opened, resulting in (irreversible) fragmentation, the resulting species being subject to further, rapid, hydrogenolysis. Though not meant as a kinetic study, it is worthwhile to discuss the observed rates in a mechanistic context. As a focal point, consider that − say, in 25 bar of H_2 − benzene conversion is 30% in 4 s at 1250 K, cf. exp. 6 and Table 2.

Since we did not conduct analogous 'pyrolysis' runs in, for example, N_2 or argon − predictably messy reactions − there is no insight into rates of methane formation at 'zero' hydrogen concentration. The effect of varying [H_2] is obvious, however, when comparing the CH_4 outputs of our earlier exp. N, (1173 K, 1 bar, 7.5 s, 3.7 mol %)[8] with that of exp. 1 (1163 K, 21 bar, 2.8 s, 23 mol %), and also exp. 4 (1249 K, 10 bar, 7.9 s, 91 mol %) and exp. 6 (same T, but 29 bar, 4.1 s, 158 mol %). It is unwarranted to derive an overall order in [H_2] from these − and our other − data, but it is clear that hydrogen promotes not only H/D exchange from deuterated benzene and (overall) isomerisation of 1,2-^{13}C benzene,[10] but also its decomposition.

e) Mechanism

In our earlier paper, a mechanistic scheme was advanced, involving equilibria between benzene, H_2, H· and various C_6H_7· radicals.[8] The essentials are reproduced in Scheme 1.[31]



Scheme 1. For detailed description of calculations, see ref.[25]
[a] Standard enthalpies of formation of **A** in kcal mol^{-1}, ref.[19] others derived by group additivity

That [H·] is present under (near) equilibrium concentrations at 1 bar has been shown before,[15] and this must also have been the case with the experiments of Zimmermann et al.[10,18] No doubt the same holds for reaction at elevated pressures. Our earlier proposal − by analogy with a suggested pathway in the reaction of cyclopentenyl radical[23] − that one or more species **A**−D on the C_6H_7· profile can add H_2 molecularly and then decompose to yield CH_3· cannot really withstand a full thermokinetic check.[22] Pathways through combination of C_6H_7· with H· are also much too slow (see Table 2). Likewise, reaction via phenyl radicals C_6H_5· − which can play an important role in combustion − cannot measurably contribute: given its (calculated) equilibrium concentration and its half-life for (unimolecular)

Table 2. Thermochemical-kinetic features for reaction of benzene/H_2 at 25 bar

Model case: benzene/H_2 = 1:12 (mol/mol), reaction time = 4 s, conversion 30 %, T = 1250 K	
[H_2] = $10^{-0.6}$ M; [H·]$_{eq}$ = $10^{-7.6}$ M ($10^{-5.6}$ bar)[16]	
[C_6H_6] = $10^{-1.7}$ M; [C_6H_7· = (**A**)]$_{eq}$ = $10^{-8.3}$ M;[19] [C_6H_5·]$_{eq}$ = $10^{-7.1}$;[20]	
k_4 = $10^{-1.0}$ s^{-1}; k_5 = $10^{5.6}$ s^{-1}	
rate of conversion of benzene:	$10^{-2.7}$ M s^{-1}
calculated rate constant for unimolecular topomerization:	$10^{-3.6}$ s^{-1} [a]
calculated rate constant for unimolecular topomerization at 850 °C (1123 K):	$10^{-5.5}$ s^{-1}
rate constant for topomerization observed in H_2 (1 bar) at 1123 K	$10^{-1.1}$ s^{-1} [b]
k_4, extrapolated to 1123 K	$10^{-2.3}$ s^{-1} [c]
rate of conversion of benzene via C_6H_5·	$10^{-5.3}$ M s^{-1} [d]

[a] Ref.[11] with log k/s^{-1} = 13 − 95/2.3RT. − [b] Ref.[10], accepting 7% conversion in 1 s. − [c] With log k_4/s^{-1} = 10.6 − 66/2.3RT, based on rate data of experiments 1, 2, 3 and 5. − [d] From ref.[21]; the rate constant for unimolecular decomposition of C_6H_5· at 1250 K is calculated to be $10^{1.8}$ s^{-1}. With [C_6H_5·]$_{eq}$ = $10^{-7.1}$ M, the calculated rate = $10^{1.8} \cdot 10^{-7.1} = 10^{-5.3}$ M s^{-1}, a factor $10^{2.6}$ below the observed rate.

decomposition,[21] rates along this pathway are several orders too low to cover the observations (Table 2).

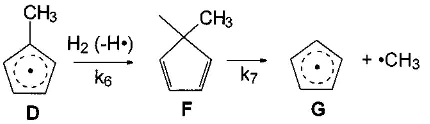
In our 'standard' experiment at 1250 K and 25 bar, 30% conversion in 4 s, the overall first-order model rate constant k_4 is close to 0.1 s^{-1}. When expressed as a unimolecular reaction of $C_6H_7\cdot$ (**A**) $k_5 = 10^{5.6}\ s^{-1}$, given the equilibrium ratio between benzene and **A** of $10^{6.6}$ (Table 2).

$$C_6H_6 \xrightarrow{(k_4)} CH_4 \tag{4}$$

$$C_6H_6 + H\cdot \rightleftharpoons C_6H_7\cdot \xrightarrow{(k_5)} CH_4 \tag{5}$$

It is worthwhile to compare these rate constants with that calculated for unimolecular automerisation of benzene − via benzvalene, for example[11] − and that for the observed isomerisation of the ^{13}C-labelled benzene in the presence of hydrogen,[10] see Table 2. While the unimolecular process is much slower than that for methane formation (showing that such a unimolecular mechanism is negligible in our case), the 'hydrogen assisted' isomerisation[10] − via $C_6H_7\cdot$ species, one way or another − is considerably faster than degradation to CH_4. As we cannot explain methane formation straight from a $C_6H_7\cdot$ species with acceptable rate parameters to cover k_5, pathways involving further hydrogenation remain as the only reasonable option.

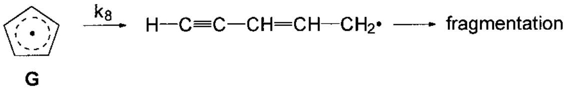
As mentioned above, molecular addition of H_2, because of entropy constraints, appears to be too slow to cover rates as expressed by k_5.[22] Much more likely in our view is that a proper $C_6H_7\cdot$ isomer (e.g. **D** in Scheme 1) may react with H_2 by regular H-transfer, as depicted in Scheme 2.[31]



Scheme 2

With realistic parameters for k_6 ($\log A_6/\text{M}^{-1}\text{s}^{-1} = 12$, $E_6 = 35$ kcal mol^{-1} [25]), $k_6 = 10^{5.9}\ \text{M}^{-1}\text{s}^{-1}$ at 1250 K, two orders of magnitude above the value estimated for molecular addition of H_2 to **D**.[22] With this value for k_6, and assigning $[\mathbf{D}]_{eq} = 10^{-8.1}$ M,[22] the estimated rate of reaction becomes $10^{5.9}\cdot10^{-8.1}\cdot10^{-0.6} = 10^{-2.8}\ \text{M s}^{-1}$, fully covering the observed rate of reaction of benzene of $10^{-2.7}\ \text{M s}^{-1}$. Note that hydrocarbon **F** has a weak C−C bond; under conditions under which even ethane is no longer stable, **E** is short-lived only, implying also that the reverse of reaction 6 is slow in comparison to reaction 7 (see Scheme 3 in the ref. section).[27]

The exact fate of cyclopentadienyl radical (**G**) (and similar species) is not known, but little speculation is necessary to conjecture that it will be subject to rapid breakdown. Species **G** will be equilibrated with cyclopentadiene (**H**). Separate experiments with **H**, in a fourfold excess of H_2, 1 bar, 10 s dwell time, already showed 50% conversion at 970 K, the reaction nearing completion at 1100 K.[29] Benzene will not yet react measurably at that temperature, (see Table 1, exp. N). Methane was a major product, with lesser amounts of C_2-hydrocarbons. The relatively high concentration of **H** resulted in a variety of other (intermediate, condensation) products as well, including cyclopentene, indene, naphthalene and benzene. In this study with benzene, pathways through hydrogenation of **G** and **H**, to cyclopentene, for example, followed by ring-opening due to C−C homolysis − are likely. Furthermore, a recent shock tube study of **H** strongly points at a direct conversion of radical **G** into a ring-opened radical species, which then decomposes to acetylene and other fragments [Equation (8)]:[30]



(8)

Even if reaction 8 requires some 60 kcal/mol activation energy (20 kcal/mol above its endothermicity), the half-life of **G** at 1250 K for this process is no more than 1 ms.

Conclusion

In conclusion, benzene is smoothly converted to high yields of methane upon reaction in an excess of hydrogen at elevated pressure (25 bar) between 1150−1250 K on a timescale of seconds. With benzene derivatives, the substituents (like Cl or CH_3) are displaced by H before degradation of benzene rings becomes significant. Our data imply that − at 1250 K − such "desubstitutions" are ca. 300−400 times faster than hydrogenolysis of benzene rings. Extrapolation of our rate/conversion data shows that essentially complete conversion of benzene into methane can be expected at $T < 1600$ K, thus under conditions that compare favourably with those of steam gasification.

The degradation of benzene is best explained by − reversible − addition of a H atom, isomerisation of (and equilibration between) $C_6H_7\cdot$ radical species including methylcyclopentadienyl (**D**), H-transfer by H_2, and loss of $\cdot CH_3$ (Scheme 2). Remaining (cyclo) C_5-species are further split into smaller molecules and radicals, ultimately leading to methane as well.

Experimental Section

Set-up: The high-pressure set-up used in this study is depicted in Figure 1. It consists of a quartz reactor (2) (Heraeus; internal diameter 10 mm, wall thickness 4 mm), placed vertically in a temperature-controlled (RKC-REX C-10) oven (4) (Heraeus ROKA 4/30, 2000 W). For safety reasons, the reactor is encased in a stainless steal pipe, flushed during the experiment with a slow stream of nitrogen, to create a nonflammable blanket. Nitrogen and hydrogen are fed through electronic mass flow controllers (Brooks 5850 TR). The pressure is measured by means of an electronic pressure meter (Rosemount, Alphaline 1511). The pressure is monitored by an adjustable dual alarm unit. Should the pressure become too high or too low, the Dräger gas pressure signal system would automatically

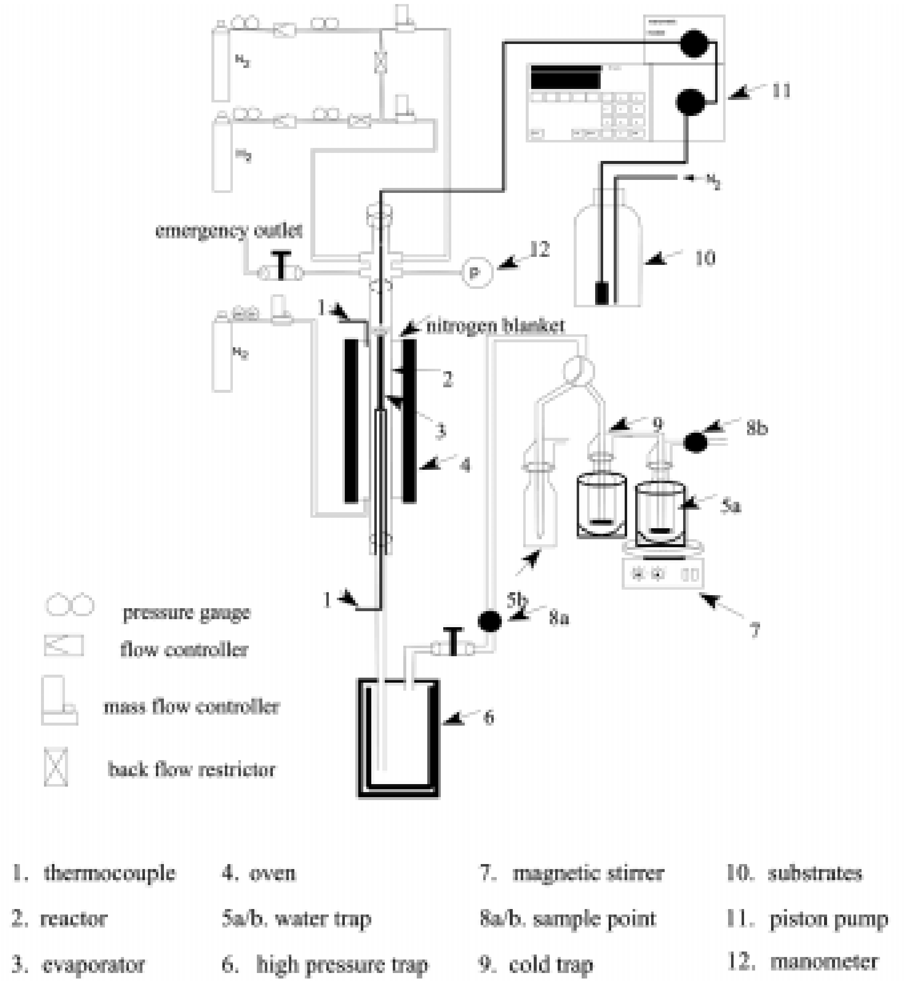


Figure 1. The high-pressure experimental set-up

substitute hydrogen with nitrogen and sound the alarm. The liquid feed (10) is delivered by two Gilson 305 pumps (11) equipped with a manometric module (Gilson 807). In order to remove any dissolved oxygen from the feed, nitrogen was bubbled through the flasks. The liquids are injected into the reactor onto a tulip-shaped evaporator (3) to obtain proper mixing with hydrogen. The temperature is measured inside the reactor as well as in 5 other locations along the system, by means of thermocouples (1) (Thermo Electric, type K) connected to a Thermo Electric, IDC-430042 indicator. The operating procedure consisted of three stages:

Firstly, the set-up was checked for leaks: if no pressure drop under maximum load was observed (50 bar), the pressure was lowered to a desired value and nitrogen was substituted with hydrogen.

After the pressure and the gas flow had stabilised, the piston pump was set to work. The "collecting time" (CT) was measured from the moment when a sharp temperature decrease was observed at the top of the evaporator (3). Closing down the substrates flow marked the end of CT. The hydrogen flow was kept constant for the next 15 minutes to allow proper elution of products.

Subsequently, hydrogen was shut down and the pressure released. Before removal of the reactor, it was flushed with nitrogen to eliminate the risk of explosion.

Analysis: The liquid products are collected in the pressurised part of the set-up in a metal vessel with a glass insert. The gaseous compounds leave the reactor (with release of the pressure) over a stainless steel regulated needle valve (Swagelok) and are bubbled through cooled pentane to condense the remaining organics. Gas samples are taken at atmospheric pressure with a syringe through a septum (8b in Figure 1) and analysed offline on a Packard model 428 gas chromatograph (GC) equipped with a Carbosphere packed column (80−100 mesh, Alltech), a methanizer (Chrompack) and a flame ionisation detector (FID). The liquid samples are analysed with GC/FID (Hewlett Packard 5890A) and GC/MS (Hewlett Packard 5970).

Both GCs (FID and MS) were equipped with 50 m × 0.32 mm CP-Sil-5 capillary columns (Chrompack).

Chemicals: The following chemicals were utilised in this study: benzene (Merck, >99.5%, distilled), chlorobenzene (Baker Analysed, 99.5%), toluene (Merck, 99.5%), bromobenzene (Baker Analysed, 99.5%), C_1/C_2 calibration mixture (CO/CO$_2$, methane through ethane 1% (v/v) each in nitrogen, Scott Speciality Gases).

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[18] In 1 bar of H_2 at 1123 K, $[H\cdot]_{eq} \approx 10^{-9.3}$ M.[16] The *per site* rate constant for displacement of D by H· is $10^{9.0}$ $M^{-1}s^{-1}$.[15] Hence, the pseudounimolecular rate constant with [H·] at equilibrium is $10^{-0.3}$ s^{-1}, to give ca. 25% conversion in 0.2−0.3 s. This compares well with ca. 50% conversion of D_2-benzene into C_6H_5D[10].

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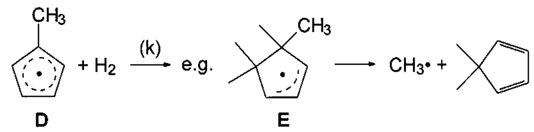
[22] Accepting Gordon's parameters for loss of H_2 from cyclopentyl to cyclopentenyl radical, (see ref [23]) as $\log A/s^{-1} = 13.5$ $E = 38$ kcal mol^{-1}, the reverse reaction will have $\log A/M^{-1}s^{-1} \approx 8$, $E \approx 24$ kcal/mol. This implies a rate constant of about $10^{4.0}$ $M^{-1}s^{-1}$ at 1250 K. Said parameters are based on a reaction entropy at 1250 K of 25 cal mol^{-1}K^{-1}. For the analogous process, cyclopentenyl ⇄ cyclopentadienyl + H_2, thermodynamic parameters are nearly the same. Extending this analogy to the rate parameters for H_2 addition, and to the methylated analogue **D**, its reaction, say, through **E** to $CH_3\cdot$ (see Scheme 3) will imply a rate which can be approached as follows: Allow $(\mathbf{D})_{eq}$ to be $10^{-8.1}$ M, slightly higher than $(\mathbf{A})_{eq}$ (Table 2). With $[H_2] = 10^{-0.6}$ M, and $k = 10^4$ $M^{-1}s^{-1}$, the rate becomes 10^4 $10^{-0.6}$ $10^{-8.1} = 10^{-4.7}$ M s^{-1}, as compared with an observed rate of $10^{-2.7}$ M s^{-1}.



Scheme 3

[23] A. S. Gordon, *Can. J. Chem.* **1965**, *43*, 570−581.

[24] Data from *NIST Standard Thermodynamic Database* at *http://webbook.NIST.gov*

[25] For H-transfers, $R\cdot + H_2 \rightarrow RH + H\cdot$, log A values of 12 are common, for R· from primary to tertiary.[17] The value for E_6 is derived as follows: from the standard heat of formation of cyclopentadiene (32 kcal mol^{-1}), and an increment of −6 kcal mol^{-1} for the methyl group, $\Delta_f H^{0}_{298}$ (**F**) = 26 kcal mol^{-1}. With a resonance energy in cyclopentadienyl radical **G** of 21 kcal mol^{-1}, the allylic C−H bond in cyclopentadiene is 77 kcal mol^{-1}.[26] Allowing for a small weakening effect, the allylic C−H bond in **F** is set at 75, implying $\Delta_f H^{0}_{298}$ (**D**) = 49 kcal mol^{-1}. Then, reaction (6) of Scheme 2 is 29 kcal/mol endothermic. By comparison with reaction enthalpies and activation energies of other H-transfer reactions, the reverse reaction (−6) will require E_{-6} of ca 6 kcal mol^{-1}, to arrive at $\log k_6/M^{-1}s^{-1} = 12-35/2.3RT$ or 5.9 at 1250 K.

[26] D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem.* **1982**, *33*, 493−532.

[27] With standard heats of formation for **F** = 26, for **G** = 57, and for $\cdot CH_3$ = 35 kcal mol^{-1}, the C−Me bond in **F** is ca. 66 kcal mol^{-1}; with $A_7 = 10^{17}$,[28] k_7 is over 10^5 s^{-1} at 1250 K. For the reverse reaction 6, accepting $k_{-6} = 10^{13-6/2.3RT}$, or ca. 10^{12} $M^{-1}s^{-1}$ at 1250 K, $k_{-6}\,[H\cdot] \approx 10^{12}\cdot 10^{-7.6} \approx 10^{4.4}$ s^{-1}, one order of magnitude less than k_7.

[28] Kinetic Data on Gas Phase Unimolecular Reactions, S. W. Benson, H. E. O'Neal, NSRDS-NBS 21, **1970**.

[29] W. Klinkenberg, R. Louw, CCE Special Report Series 87−01, Leiden University, **1987**.

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[31] As pointed out by a referee, species C may (also) lose a H atom to yield fulvene − which then can give D by (re)addition of H. The 34 kcal/mol difference in the heats of formation of fulvene and benzene implies a level of fulvene under (pseudo) equilibrium conditions at 1250 K of only 1 ppm based on benzene. If present − and surviving trapping etc. − this has escaped our attention on analysis. A thermokinetic assessment based on reasonable rate parameters, hence with log A values for analogous reactions,[17] shows that direct isomerization **C** → **D** and the pathway through fulvene are likely to be competitive under the conditions used.

Received November 14, 2000
[O00581]