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A Mechanistic Study on the Catalytic Combustion of Benzene and Chlorobenzene

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The catalytic combustion of benzene (C_6H_6), hexadeuterobenzene (C_6D_6), and chlorobenzene (PhCl) was investigated under various conditions on a 2 wt% Pt/γ–Al_2O_3 catalyst. Typical conditions were 1000 ppm of organics in the inflow, contact times of ~0.3 s, and 16% O_2 in nitrogen at ~1 bar.

Benzene as such reacted very easily, much faster than PhCl per se, with $T_{50\%}$ only ~145°C. With C_6H_6/C_6D_6 the kinetic isotope effect ranged from 2.5 to 1.5 between 130°C and 160°C. Cocombustion of C_6H_6/C_6D_6/PhCl led to lower rates for the benzenes but higher rates for PhCl, to give comparable $T_{50\%}$ values of around 250°C. Between 200°C and 300°C k_H/k_D was ~1.6. Comparable results were obtained with C_6H_6/C_6D_6/C_2Cl_4. In this case the side reaction, chlorination, is visible from formed C_6H_5Cl and C_6D_5Cl; it appears to occur without H/D isotope effect.

If the O_2 concentration were increased from 8 to 14% combustion rates for C_6H_6 were increased to a limited extent; between 153°C and 213°C the order in O_2 is ~0.2. Also the conversion of PhCl was measured at 328°C with O_2 partial pressures ranging from 1 to 16%; above 4% the conversion decreased, while the level of polychlorinated benzenes ($PhCl_x$) increased almost fivefold, from 0.55 to 2.5% of the PhCl input, when [O_2] was raised from 4 to 16%.

Cocombustion of PhCl and heptane gave much higher rates for the former, while the output of $PhCl_x$ was greatly reduced; at 16% O_2 from 2.5% for combustion of PhCl per se, to 0.25% with 2.3 mol of heptane per mole PhCl in the feed. Water had a much less beneficial effect.

The mechanism(s) are discussed on the basis of the operation of (at least) two different types of active sites. In the absence of chlorine a C–H(D) bond in sorbed benzene is split, and the surface-bound H and phenyl moieties are oxidized, most likely via phenoxyl entities which are subject to rapid breakdown. Chlorine—e.g., formed from added PhCl upon its combustion—acts as a poison, the more so when using PhCl alone. Then, a slow C–Cl bond activation occurs on another type of site. Added heptane, through its hydrogen, can remove Cl from the metal surface and regenerate the sites for sorption and C–H bond activation. The side reaction, (oxy)chlorination, is best described as recombination of a surface-bound phenyl entity with—electrophilic—chlorine, presumably at an oxidized Pt site.

Key Words: **kinetic H/D isotope effect; chlorobenzene; chlorination; benzene; Pt/Al_2O_3; combustion; mechanism.**

1. INTRODUCTION

Used, waste, or obsolete (chlorinated) organic compounds and materials must be properly disposed of. Well-managed incineration is feasible, but costly due to the advanced pollution control devices needed to prevent, e.g., emission of dioxins. Alternative treatment options for (dilute) chlorine containing organic wastes are hydrogenolysis (1, 2) or catalytic oxidation to (ideally) HCl, H_2O, and CO_2 (3–5). The best method for treating waste gases greatly depends on the composition. Oxidation—thermal or catalytic—may well be more appropriate (and more economical) than hydrogenation, especially if dilute oxygen-containing gases have to be treated (6).

Generally chromium oxide is found to be a very active catalyst for the combustion of chlorinated hydrocarbons; other metal oxides which are known to be active are those of copper (6), manganese (7, 8), and vanadium (9). In treating chlorine containing waste gases a serious drawback is the volatility of some of the metal(oxy)chlorides which can be formed: chromium oxychloride (CrO_2Cl_2), for example, has a boiling point of only 117°C and $CuCl_2$ volatilizes at 600°C. Their formation—and elution—will shorten the lifetime of these catalysts and seriously limits their applicability (10, 11).

Supported platinum and palladium catalysts are frequently applied for complete conversion of halogen-free organics. Pd is known to be the most active in CH_4 oxidation and Pt is more active in the combustion of higher hydrocarbon homologues (12–14). Organic chlorine (OCl) is a well-known poison for noble metal catalysts. The catalytic activity is decreased due to the high bonding energy

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of chlorine after dissociation on the surface (4, 15), which results in chlorination of the catalyst.

The addition of 1% H_2O to the feed stream resulted in a better performance: $T_{50\%}$ was for several supported Pt catalysts reduced by some 20°C and the polychlorinated benzene ($PhCl_x$) levels were lowered, for example, on Pt/ZrO_2 by a factor of 5 when compared to an experiment with PhCl alone (3). Addition of *n*-heptane (e.g., several moles/mole of PhCl) was also found to improve the performance of a 2 wt% $Pt/\gamma{-}Al_2O_3$ catalyst during the combustion of PhCl. The temperature to reach full conversion was much lower and the formation of byproducts (mainly $PhCl_x$) was greatly reduced (16). Other alkanes or alkenes led to similar results, but benzene or CO had a much smaller effect.

The performance of supported Pd with respect to PhCl is poor: rates are lower than with Pt and there arise more $PhCl_x$ byproducts (3). Addition of H_2O led to lower rates and had little effect on the $PhCl_x$ production. Efforts to improve the performance of supported Pd on alumina and zirconia are under way and include the use of methane as a mediator (De Jong *et al.*, unpublished results).

Insight into the mechanism of the conversion of benzene and PhCl can be obtained through competition experiments with deuterated homologues (17, 18). Previously the kinetic isotope effect during the catalytic combustion of a $PhCl/C_6D_5Cl$ mixture on 2 wt% $Pt/\gamma{-}Al_2O_3$ in the temperature region of 250–310°C was found to be close to unity (19). That C–H(D) bond fission is not a key rate-determining step suggests that C–Cl bond fission is important. In the presence of heptane—with smooth reaction now between 190° and 210°C—the isotope effect was ∼1.5 (19). From experiments with $^{16}O_2/^{18}O_2$ it was found that O_2 dissociatively adsorbs on Pt at temperatures above −173°C (20). Recent studies with CH_4/CD_4 and $^{16}O_2/^{18}O_2$ showed that combustion on PdO catalysts occurs via irreversible dissociation of O_2 (13).

The present work deals with the catalytic combustion of (chlorinated) benzenes on a 2wt% $Pt/\gamma{-}Al_2O_3$ catalyst. Several factors have been varied to find their impact on rates and products. The influence of the O_2 concentration on the combustion of C_6H_6 per se and in the presence of PhCl has been determined. Next, the latter compound was treated in the presence of heptane at various O_2 concentrations. We also thought it of interest to investigate the behavior of C_6H_6/C_6D_6 in the presence of PhCl: mutual influences on rates of combustion—including the kinetic isotope effect, k_H/k_D, for the benzenes—and on possible (poly)chlorination. To this end, three mixtures of C_6H_6 and C_6D_6 were used, with H/D ratios of 1 : 1, 1 : 3, and 3 : 1. In addition, experiments with C_6H_6/C_6D_6 in the presence of C_2Cl_4 as a chlorine source are described with the focus on the (oxy)chlorination reaction of the benzenes.

2. METHODS

2.1. *The Online Setup*

The computer-controlled setup was described in detail by Van den Brink *et al.* (5). In short, the (liquid) model compounds were introduced through two thermostatted impinger vessels, evaporated by bubbling through N_2 (Air Products 99.9%). The gas flows were controlled by electronic mass flow controllers (Brooks 5850 TR). The reactor was a vertical quartz tube with a quartz filter carrying the catalyst, connected to a GC (Hewlett Packard 5890 Type II) by heated (>180°C) glass-lined stainless steel tubing. Samples were injected on a capillary (CP SIL 5 CB, 50 m × 0.32 mm, film thickness 0.4 μm) and a packed (Carbosphere 80–100 mesh) column by two six-port microinjection valves (Valco C6WT-HC). The packed column was connected to a methanizer to convert available CO/CO_2 into CH_4, and a flame ionization detector (FID) was used to quantify these. The capillary column was split in two and connected to a FID (for quantification of organic products) and an electron capture detector (ECD, for chlorinated products). Identifications were performed with an offline GC (HP 5890 series II) equipped with a capillary column (Chrompack CP-SIL, 5CB, 50 m, d 0.32 mm, film 0.4 μm), an automatic injector (HP 6890 Series), and a mass selective detector (HP5972).

The total flow was typically 0.27 mol h^{-1}, which yielded a residence time (τ_{void}) of 0.3 s at 200°C. The concentrations of the substrates varied somewhat. Previous experiments with PhCl per se showed that conversions and relative amounts of byproducts were independent of the initial PhCl concentration.

2.2. *Catalyst*

A 2 wt% $Pt/\gamma{-}Al_2O_3$ catalyst was prepared following the homogeneous deposition precipitation method as described by Geus (21). For 10 g catalyst, 9.80 g $\gamma{-}Al_2O_3$ (Degussa C) was suspended in 250 ml water. 0.308 g $H_2[Pt(OH)_6]$ (Johnson Matthey, 62.5% Pt) was dissolved in 3 ml hot nitric acid and added to the suspension under continuous stirring. Then 10 g urea was added and the temperature was raised to ca. 80°C. The suspension was stirred for 15 h. Due to slow decomposition of urea the pH increased from 2 to 8, which caused the Pt precursor to precipitate on the $\gamma{-}Al_2O_3$ support. The suspension was filtered off, washed with demineralised water, and dried overnight at 90°C. After calcination for 3 h in flowing air at 600°C and crushing, the sieved fraction of 150–300 μm was used. The dispersion of the Pt particles measured with CO chemisorption (Quantasorb Jr.) was found to be ∼20%. The mean particle size was determined by transmission electron microscopy using a Philips CM 30 microscope and was found to be 6.2 (3).

2.3. *Calculation of Isotope Effects*

The isotope effect at a given temperature is equal to the relative rate of the H-containing compound divided by that of the deuterated homologue. If the Arrhenius equation is applied, if the number of active sites on the catalyst for both homologues is the same, and if no H tunneling occurs, $A_H = A_D$, which results in

$$\frac{k_H}{k_D} = \exp\left[\frac{(E_{aH} - E_{aD})}{R \cdot T}\right]. \quad [1]$$

E_a's are activation energies in cal mol^{-1} and R is the gas constant (1.99 cal mol^{-1} K^{-1}). The maximum possible isotope effect at a given temperature T can be calculated from the difference in zeropoint vibrational energy, $E_{aH} - E_{aD} =$ 1.15 kcal mol^{-1} (22). To prevent mass-transfer limited rates, conversions should be below 70%.

3. RESULTS

3.1. *General Features*

Knowing that cofeeding a hydrocarbon such as heptane is beneficial for the combustion of PhCl on 2%Pt/γ–Al_2O_3 (5) we have first repeated that approach and compared the effect with that of adding water vapor, for temperatures between 242°C and 493°C. Results are collected in Table 1.

With the amount of H_2O added to the inflow the levels of $PhCl_x$ are somewhat lowered; rates of conversion of PhCl are also increased ($T_{50\%}$ is reduced by over 20°C) and the patterns of $PhCl_x$ look quite the same.

With added heptane the byproduct formation, as expected, is strongly decreased; the temperature with a maximal $PhCl_x$ output is lowered from around 370°C for PhCl alone to 290°C with heptane. Above 370°C there are no byproducts found in the outflow. The very low output of $PhCl_x$ consists of essentially only $PhCl_2$—unlike the results for reactions without heptane. Heptane itself does not lead to chlorinated byproducts: chlorinated C_1's are seen at best only at ultratrace levels. The beneficial effect of heptane cannot be due to the (extra) H_2O, as the 700 ppm of heptane will yield at best 5600 ppm, which is lower than the amount in the experiment with added H_2O (7000 ppm). Rather, heptane promotes the combustion of PhCl through removal of chlorine from the catalyst surface by its hydrogen (4).

TABLE 1

Formation of $PhCl_x$ on 2% Pt/γ–Al_2O_3 during the Combustion of PhCl, Alone and in the Presence of H_2O or *n*-Heptane (C_7H_{16})[a]

T [°C]	PhCl [%]	PhCl/H_2O [%]	PhCl/C_7H_{16} [%]
49	0	0	0
242	0.8	n.d.	0.1
292	2.7	0.9	0.4
333	7.3	4.3	0.1
372	12.2	8.7	n.d.
411	7.0	5.0	n.d.
452	2.0	1.7	n.d.
493	0.7	0.9	n.d.

[a] 300 mg catalyst; total flow 0.27 mmol h^{-1}, 16% O_2, and N_2 as make-up gas. PhCl: 320 ppm alone and in presence of H_2O (7000 ppm) or 700 ppm C_7H_{16}. $PhCl_x$ outputs are expressed as % of PhCl input; n.d. = below detection limit of ~ 0.05%.

3.2. *Influence of the Oxygen Concentration*

In catalytic combustion noble metals are sensitive to chlorine poisoning (23–25). Also MeO_xCl_y species are likely to play a role in the formation of $PhCl_x$. It is important to know the influence of $[O_2]$ on the catalyst performance, as a function of structure and chlorine level. The present section deals with the effect of $[O_2]$ on the combustion rates of benzene (C_6H_6), chlorobenzene (PhCl), and PhCl in presence of heptane.

3.2.1. Effect of $[O_2]$ on the conversion of C_6H_6. The combustion of benzene on 2 wt% Pt/γ–Al_2O_3 has been studied at various O_2 partial pressures. For these experiments 30 mg Pt/Al_2O_3 catalyst diluted with 270 mg γ-Al_2O_3 (pretreated at 300°C) without the metal was used in order to reduce the otherwise high reaction rates. On the undiluted 2% Pt catalyst combustion was already perceptible at 120°C, while full conversion was reached at 160°C. For the diluted catalyst these temperatures were 130°C and >220°C, respectively. The O_2 concentration was varied from 8 to 16%. Figure 1 depicts the changes in reaction rate in double logarithmic plots. The conversions for all data points were between 20 and 80%.

The O_2 concentration has a small but distinct effect. When $[O_2]$ is increased from 8 to 14% an increase in the reaction rate is found, but with 16% ($\ln([O_2]) = -1.83$) the conversions are a bit lower. For example, at 174°C the conversion increases from 45% (8% O_2) to 52% (14% O_2) while the conversion for 16% O_2 was found to be 50%. Presumably, below 14% the amount of O_2 is rate limiting and above this concentration this holds for C_6H_6. The lines drawn through the data points from 8 to 14% O_2 define the experimental reaction order. From the slopes of the four lines an order in $[O_2]$ of 0.2 can be calculated.

3.2.2. Influence of $[O_2]$ on the conversion of PhCl. To gain a better insight into the performance of Pt in the catalytic combustion of PhCl, the O_2 concentration has been varied from 1 to 16% with N_2 as make-up gas. Figure 2 shows the conversion of PhCl and the total production of $PhCl_x$ (in equivalents of chlorine based on input of PhCl) as a function of $[O_2]$ at 328°C on 2% Pt/γ–Al_2O_3. Note that per PhCl molecule 7 O_2 molecules are needed for a full conversion into CO_2, H_2O, and HCl, which is equivalent to ~0.22% $[O_2]$ of the gas composition.

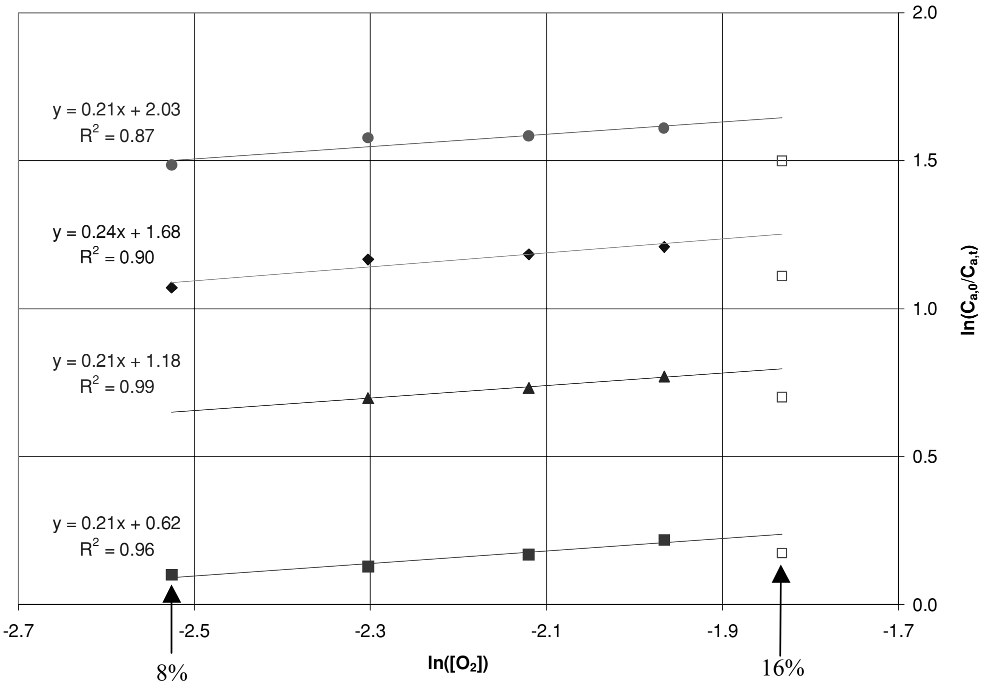

FIG. 1. Observed reaction rates for C_6H_6 conversion as a function of the O_2 concentration on 2% Pt/γ–Al_2O_3 at 153°C (■); 174°C (▲); 195°C (◆); 213°C (●); 16% O_2 at various temperatures (□). Inflows: C_6H_6 1950 ppm, $N_2 + O_2$ 0.27 mol h^{-1}; $\tau_{void} \sim 0.36$ s at STP, 1 atm and 25°C.

The conversion of PhCl clearly depends on [O_2]. The highest activity of the catalyst is found around 4% [O_2] with a conversion close to 98% at 328°C. If the O_2 concentration is increased to 16% the conversion decreases to 82%. With 1% O_2 the conversion is 60%, while the needed amount of O_2 is less than one-quarter of its input.

The level of chlorinated byproducts also changes with the O_2 concentration. The $PhCl_x$ output rises at increasing [O_2] from 0.3% at 1% O_2 to 2.5% at the highest used [O_2]. Also a change in pattern was observed from lower chlorinated products at low [O_2] to higher chlorinated analogues at 16% O_2. For PhCl a reaction order in [O_2] has been

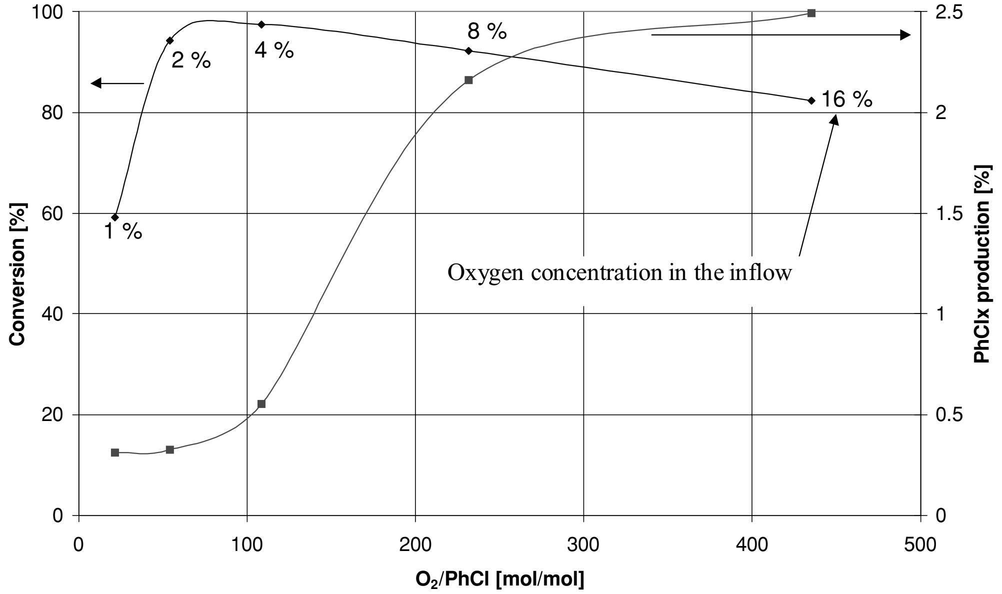

FIG. 2. Conversion of PhCl at various O_2 partial pressures at 328°C on 2% Pt/γ–Al_2O_3: PhCl conversion (◆), total $PhCl_x$ production (■). Inflows: PhCl 320 ppm, $N_2 + O_2$ 0.27 mol h^{-1}; $\tau_{void} \sim 0.36$ s at STP. $PhCl_x$ production is based on the total chlorine input.

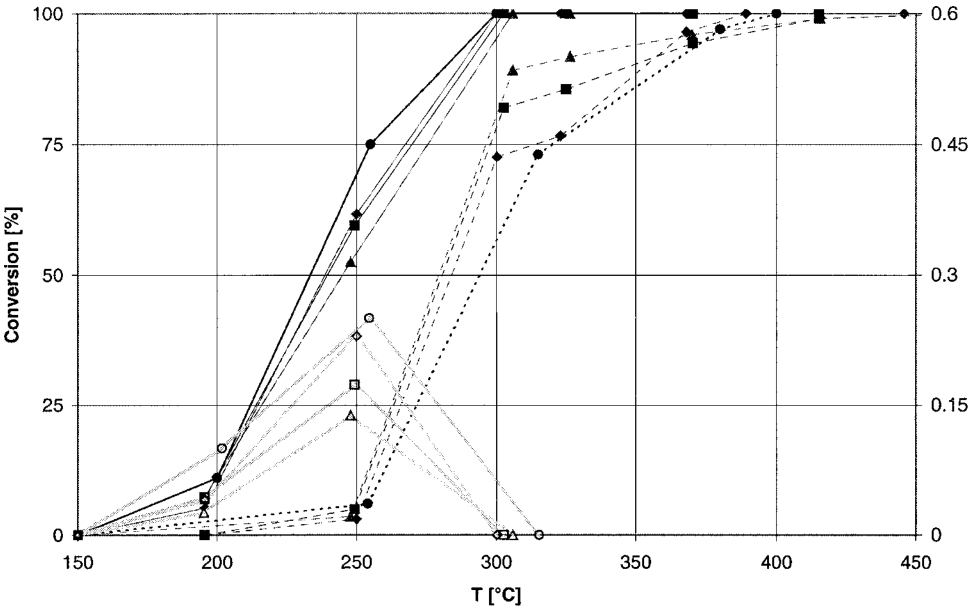

FIG. 3. Conversion of PhCl (—) and of heptane (- - -), and PhCl$_x$ production (· · ·), as a function of O_2 concentration, 8% O_2 (▲), 11% O_2 (■), 13% O_2 (◆), 16% O_2 (●). Inflows: PhCl 300 ppm, heptane 700 ppm, $N_2 + O_2$ 0.27 mol h^{-1}; $\tau_{void} \sim 0.36$ s at STP.

measured in a way analogous to that for benzene. When the O_2 concentration was changed from 4 to 16% and the observed reaction rate at a common temperature was plotted as in Fig. 1, a straight line resulted, from which an O_2 order of –1.4 was calculated, in contrast with that for benzene (0.2).

3.2.3. Influence of [O_2] on conversion of a mixture of PhCl and heptane. As was shown previously by Van den Brink, added heptane accelerates the conversion of PhCl and lowers the amount of byproducts (4). To see if oxygen plays a part an experiment was performed with constant heptane and PhCl input levels while the O_2 concentration was varied from 8 to 16%. The respective conversions and PhCl$_x$ outputs are plotted in Fig. 3.

As expected, heptane clearly promotes the catalytic oxidation of PhCl, consonant with the earlier observation of Van den Brink *et al.* (4). Whereas (with 16% O_2) the conversion of neat PhCl is only 82% at 328°C (Fig. 2), with added heptane its reaction is complete already at 300°C—also with negligible output of PhCl$_x$ (Fig. 3). The same rates (conversions) are found at roughly 60°C lower temperatures. With increasing [O_2] the conversion of PhCl increases slightly, in a way not unlike that for benzene (Section 3.2.1). The selectivity to PhCl$_x$ does not seem to change much; in 16% O_2, at ca. 250°C, the PhCl conversion is 75%, with ~0.25% PhCl$_x$ as an output. This is a factor of 10 less than the 2.5% from the reaction with PhCl only (Fig. 2). For 8% O_2 these values are ~52% and 0.14%, respectively.

The presence of PhCl slows down the conversion of heptane; the temperature needed to reach its full conversion is increased by more than 200°C. When the O_2 concentration is lowered from 16 to 8% the conversion of heptane appears to increase to some extent.

3.3. Combustion of C_6H_6 and C_6D_6 on 2%Pt/γ–Al_2O_3

Previously Van den Brink *et al.* (19) briefly studied the combustion of C_6H_6/C_6D_6 (1:1) on a 2 wt% Pt/γ–Al_2O_3 catalyst and found a kinetic isotope effect of around 2 between 130°C and 165°C. To obtain a better insight into the magnitude of k_H/k_D and its temperature dependence a series of experiments was performed with the same inflow mixture, mostly with the 2% Pt/γ–Al_2O_3 catalyst diluted by 90% γ–Al_2O_3. For comparison in some cases the "pure" 2 wt% Pt on γ–Al_2O_3 catalyst was used. The conversions of both benzenes were kept between 5 and 70%, to minimize errors and to avoid the diffusion-controlled regime as much as possible (Fig. 4).

The line for the maximal isotope effect at various temperatures is based on a difference in zeropoint vibration energy between a C–H and a C–D bond of 1.15 kcal mol^{-1}. The experimental data are roughly half of these values. Between 130°C and 160°C, k_H/k_D ranges from ca. 2.5 to 1.5; this is in fair agreement with the "provisional" value of 2 mentioned above (19). Remarkably, between 150°C and 180°C k_H/k_D is fairly constant at 1.4–1.5.

Throughout this series, H/D exchange between ("unreacted") benzenes was insignificant. This is consonant with earlier observations (19); H/D exchange—occurring on the alumina—will be negligible below 250°C; hence catalytic combustion (on Pt) is very much faster.

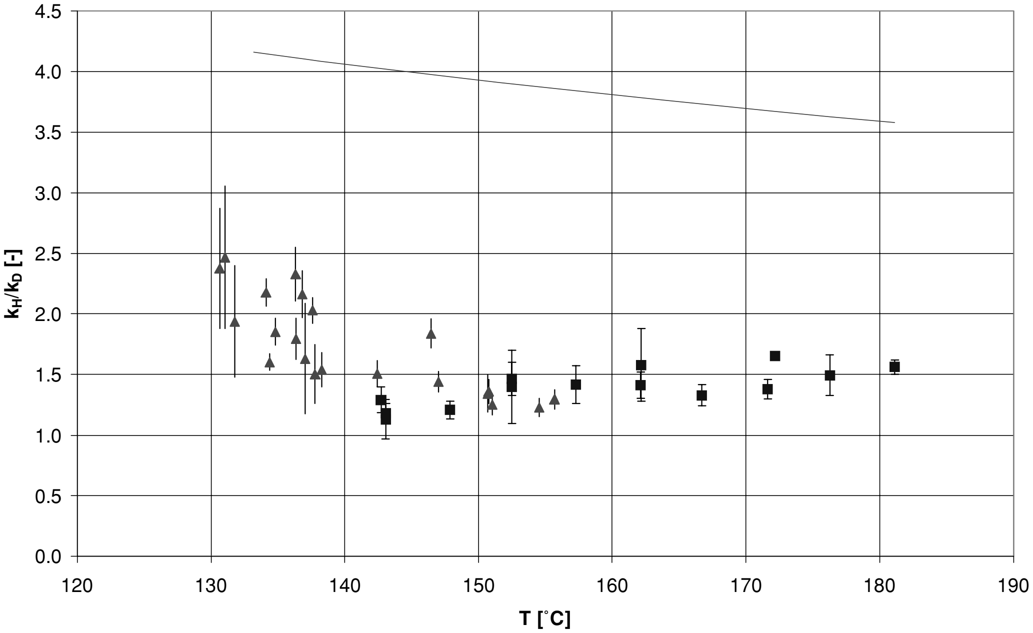

FIG. 4. Kinetic isotope effect for combustion of C_6H_6 and C_6D_6 on 2 wt%Pt/γ–Al_2O_3 (▲) or the same compound diluted to 10% with γ–Al_2O_3(■); theoretical maximum (—).

3.4. Isotope Effects in Presence of Chlorine

3.4.1. Combustion of C_6H_6 and C_6D_6 in presence of PhCl. Catalytic combustion of (deuterated) benzene undoubtedly will involve breaking of C–H(D) bonds. With PhCl the situation is less simple: For neat PhCl/C_6D_5Cl, $k_H/k_D \sim 1$ (20), but when heptane is added k_H/k_D becomes ~1.5 in an altogether faster process (Section 3.2.3). Kinetic-mechanistic focus appears to shift from (apparent) C–Cl bond activation to C–H(D) bond fission. So, the presence or absence of chlorine (organic or mineral, after reaction) is an important factor. In this light we have investigated the behavior of C_6H_6/C_6D_6 in the presence of PhCl: mutual influences on rates of combustion including k_H/k_D for the benzenes; furthermore, possible chlorination could give rise to C_6D_5Cl, and/or to H/D scrambled $PhCl_x$. Previously H/D exchange was found to be negligible in the absence of the catalyst (19). Three mixtures of C_6H_6 and C_6D_6 were prepared, with H/D ratios of 1 : 1, 1 : 3, and 3 : 1. The results are shown in Fig. 5.

The three conversion plots are comparable. Remarkably, PhCl reacts almost as fast as the benzenes (the latter with a kinetic isotope effect dealt with in Section 3.4.2). The

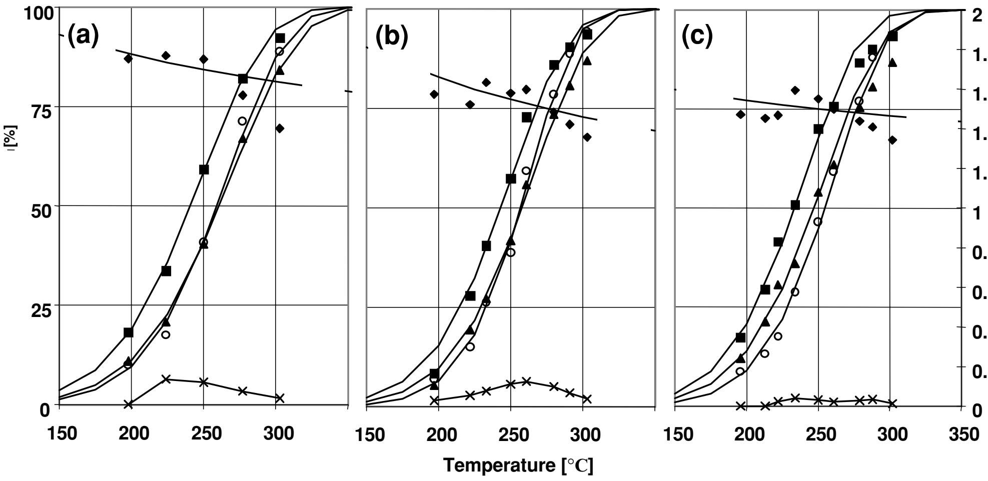

FIG. 5. Conversion of C_6H_6, C_6D_6, and PhCl on a 2 wt% Pt/γ–Al_2O_3 catalyst: (a) 1 : 1 450 ppm C_6H_6, 460 ppm C_6D_6, and 340 ppm PhCl. (b) 1 : 3 270 ppm C_6H_6, 840 ppm C_6D_6, and 360 ppm PhCl. (c) 3 : 1 700 ppm C_6H_6, 240 ppm C_6D_6, and 280 ppm PhCl. C_6H_6 (■), C_6D_6 (▲), PhCl (○), C_6D_5Cl output (% on converted C_6D_6) (x), k_H/k_D (◆); see Section 3.4.2. Inflows: Total 0.27 mol h^{-1}, 16% O_2 and N_2 as makeup; $\tau_{void} \sim 0.36$ s at STP.

TABLE 2

Kinetic Isotope Effect for C_6H_6, C_6D_6, and PhCl Mixtures on 2 wt% Pt/γ–Al_2O_3

Temp. (°C)	k_H/k_D[a] 1 : 1	k_H/k_D[b] 1 : 3	k_H/k_D[c] 3 : 1	k_H/k_D[d] Max.
198	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	3.4
213	—	—	1.5 ± 0.1	3.3
222	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	3.2
234	—	1.6 ± 0.1	1.5 ± 0.2	3.1
250	1.7 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	3.0
261	—	1.6 ± 0.1	1.5 ± 0.1	3.0
279	1.5 ± 0.1	1.4 ± 0.1	1.4 ± 0.1	2.9
288	—	1.4 ± 0.1	1.4 ± 0.1	2.8
302	1.5 ± 0.1	1.4 ± 0.1	1.4 ± 0.1	2.7

[a] Series (A) Fig. 5, 1 : 1 450 ppm C_6H_6, 460 ppm C_6D_6, 350 ppm PhCl.

[b] Series (B) Fig. 5, 1 : 3 270 ppm C_6H_6, 840 ppm C_6D_6, 360 ppm PhCl.

[c] Series (C) Fig. 5, 3 : 1 700 ppm C_6H_6, 240 ppm C_6D_6, 280 ppm PhCl.

[d] Maximal isotope effect (in absence of H "tunneling") based on a difference in C–H and C–D bond energies of 1.15 kcal mol^{-1}.

combustion of C_6H_6 and C_6D_6 is clearly inhibited due to the presence of chlorine. Under otherwise identical conditions, $T_{50\%}$ for benzene per se would be around 145°C (with 100% reaction achieved at 160°C), some 80°C less than the ca. 240°C seen in Fig. 5. Conversely, the rate of conversion of PhCl admixed with the benzenes is higher than when reacted neatly; $T_{50\%}$ values differ by some 45°C (5). All starting compounds are converted below 350°C, while $PhCl_x$ were still found above this temperature.

Due to the presence of PhCl it is only possible to follow the chlorination of C_6D_6. Its monochlorinated product C_6D_5Cl becomes detectable by online GC-FID at 200°C and vanishes above 300°C. The highest level is located around 250°C and reaches a selectivity of over 5% (based on converted C_6D_6). At higher temperatures, in situ formed C_6D_5Cl will also be oxidized with a rate constant close to that for PhCl, if k_H/k_D is also ~1 for (deuterated) chlorobenzenes admixed with the benzenes. The C_6D_5Cl levels are in line with the C_6D_6/C_6H_6 inputs. A concentration of 840 ppm C_6D_6 (*re* B, Fig. 5) resulted in 19 ppm C_6D_5Cl at 250°C, while a concentration of 240 ppm C_6D_6 (C, Fig. 5) led to only 6 ppm C_6D_5Cl. With 460 ppm C_6D_6 in the inflow mixture 12 ppm C_6D_5Cl was produced.

3.4.2. Isotope effect. From the data in the previous section kinetic isotope effects have been calculated. Results are collected in Table 2 and plotted in Fig. 5.

An overall isotope effect of ca. 1.6 ± 0.1 is found for C_6H_6 and C_6D_6 in the presence of PhCl. There is at best only a small tendency for k_H/k_D to decrease with increasing temperature (see also Fig. 5). This result can be compared with those for C_6H_6/C_6D_6 in the absence of PhCl (see Fig. 4) at considerably lower temperatures. Then there is no "perfect" connection but the values (~1.5 ± 0.1 between 150°C and 180°C, and 1.6 ± 0.1 between 200°C and 300°C) do not reveal an important mechanistic change either.

3.4.3. $PhCl_x$ production. In the series of experiments (A)–(C), (see Section 3.4.1 and Fig. 5) higher chlorinated derivatives $PhCl_x$ are also formed. Quantified by online ECD, detectable levels arose above ~170°C. Outputs and compositions for reactor temperatures up to 302°C are depicted in Fig. 6.

From Table 1 it is seen that 320 ppm of PhCl alone gave rise to ~10% yields of $PhCl_x$ at $T \sim 330$–410°C. This is mostly $PhCl_2$, and hence equivalent to ~15 ppm. In series (A)–(C), plateau values are 0.5–0.6 ppm, a factor of 25 lower, also at lower temperatures. For the higher chlorinated benzenes it was not possible to distinguish between the deuterated and the nondeuterated $PhCl_x$. If, however, the concentration of C_6D_5Cl is taken to be the ruling factor in the formation of deuterated $PhCl_x$, the highest concentration (20 ppm, see Fig. 5) would result in a 2–3% level for

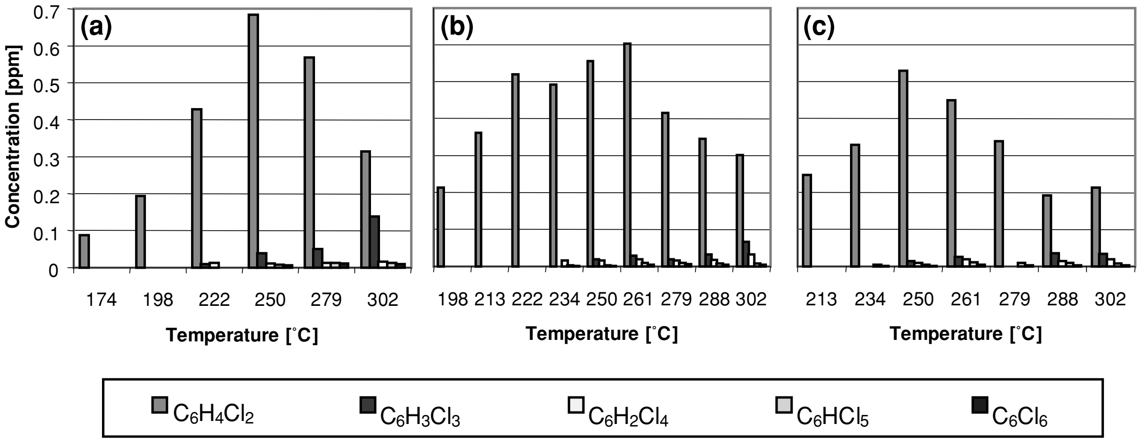

FIG. 6. Production of $PhCl_x$ in series (A)–(C); compare Fig. 5. Inflows: Total 0.27 mol h^{-1}, 16% O_2 and N_2 as makeup; $\tau_{void} \sim 0.36$ s at STP. (a) $C_6H_6/C_6D_6 = [1:1]$. (b) $C_6H_6/C_6D_6 = [1:3]$. (c) $C_6H_6/C_6D_6 = [3:1]$.

$C_6D_4Cl_2$, below the ECD detection limit. For this reason offline analysis using GC-MS was performed to determine the isotopic composition of the higher chlorinated benzenes.

3.4.4. Isotopic composition of $PhCl_x$. As mentioned earlier, in the catalytic combustion of C_6H_6/C_6D_6 there is no measurable H/D exchange in the recovered benzene. Reactions involving C_6H_6/C_6D_6/PhCl give rise to small proportions C_6D_5Cl, due to (oxy)chlorination of C_6D_6 (compare Fig. 5). In series (B), with 1 : 3 C_6H_6/C_6D_6, the highest yield of C_6D_5Cl is almost 20 ppm at 260°C, or ca. 4% on the input of C_6D_6. To find out if in the PhCl fraction H/D scrambling is perceptible, a sample *re* conditions (A), at 277°C, was collected in a cold trap over a 3-h period, and analyzed by GC-MS.

The corrections applied for $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ ratios are based on the measured abundances of the masses C_6D_5Cl +1 and +2, respectively. This resulted in a $^{13}C/^{12}C$ ratio of 1.7% per carbon, whereas the $^{37}Cl/^{35}Cl$ ratio was ~1 : 2.5. These ratios were used to calculate possible H/D exchange levels.

As a result, only a small degree of H/D exchange was found, with an abundance of C_6HD_4Cl of 6.5% relative to C_6D_5Cl, or ~0.8 ppm vs ca. 12 ppm in the outflow; $C_6H_2D_3Cl$ could not be detected. Due to the relatively high PhCl level of ca. 100 ppm (~70% of the input of 340 ppm is converted) the abundance of C_6H_4DCl was below the detection limit of the isotope analysis.

For higher chlorinated products only meta- and para-$PhCl_2$ were above the detection limit, with a ratio of 2 : 3; sum, ca. 0.6 ppm (see Fig. 6, left). Isotopic analysis as described above revealed that for both isomers the d_4/d_0 ratio is ca. 0.18. This is ca. 1.5 times the ratio of C_6D_5Cl/PhCl (12 vs 100 ppm), suggesting that the (further) chlorination of the chlorobenzenes has an inverse kinetic H/D isotope effect. This is dealt with again in Section 3.5. Note that the level of $C_6D_4Cl_2$ ($0.18/1.18 * 0.6$ or ~0.09 ppm) is ca. 0.0075 times that of the (12 ppm of) C_6D_5Cl, whereas the ratio of C_6D_5Cl in the output was ca. 9% of that of the remaining C_6D_6. One could ascribe the factor ~12 difference to a retarding effect of the chlorine substituent, but it should be noted that the situation—in terms of rate determining factors—is much more complex than that in "regular" homogenic aromatic substitution.

3.5. Conversion and (Oxy)chlorination of C_6H_6/C_6D_6 in the Presence of C_2Cl_4

To gain a better insight into the mechanism of the chlorination reaction, a mixture of C_6H_6, C_6D_6, and C_2Cl_4 was combusted in the usual way, on the 2 wt% Pt/γ–Al_2O_3 catalyst. Conversion curves and outputs of the chlorobenzenes are shown in Fig. 7, for the inflows mentioned.

When compared with data on the benzenes as such, rates are lower. Now C_6D_6 shows 75% conversion at 274°C, whereas in experiments as described in Section 3.3 the same conversion is reached at a ca. 130°C lower temperature. The relative rates of C_6H_6 and C_6D_6 again reveal a kinetic isotope effect, of 1.3 ± 0.1, in fair agreement with the value of ca. 1.5 reported in Table 2 for reaction together with PhCl. C_2Cl_4 does react also around 300°C, but for its complete conversion, temperatures above 500°C are required. Above 200°C both C_6H_5Cl and C_6D_5Cl are detected.

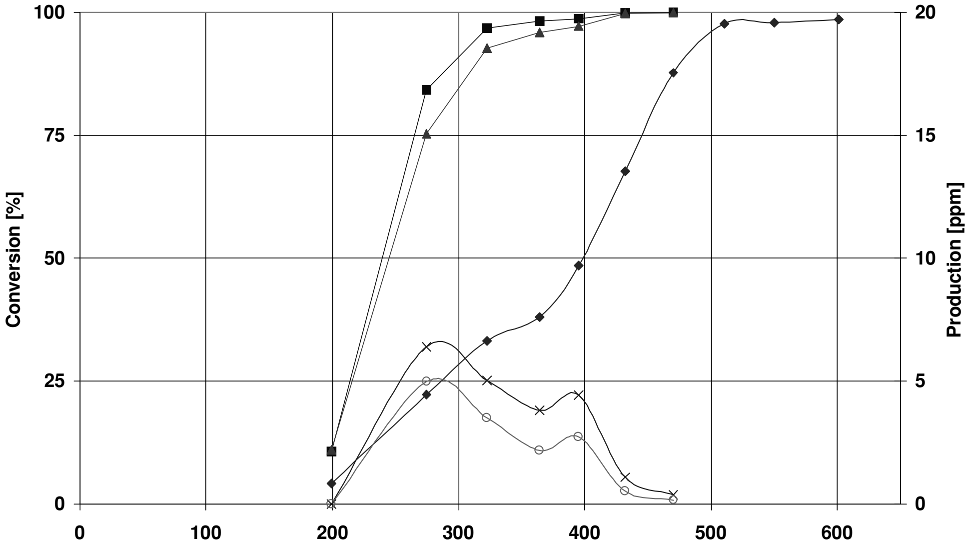

FIG. 7. Conversion of C_6H_6 and C_6D_6 in the presence of C_2Cl_4 on 2 wt% Pt/γ–Al_2O_3. C_6H_6 (■), C_6D_6 (▲), C_2Cl_4 (◆), C_6H_5Cl (production ppm) (○), and C_6D_5Cl (production ppm) (*x*). Inflows: C_6H_6 900 ppm, C_6D_6 830 ppm, C_2Cl_4 235 ppm; total 0.27 mol h^{-1}, 16% O_2 and N_2 as makeup; $\tau_{void} \sim$ 0.36 s at STP.

In the measured outputs of the chlorobenzenes, the ratios C_6H_5Cl/C_6D_5Cl are consistently below 1; at 274°C (with 75–85% conversions of the benzenes), the ratio is 0.78, and, for example, at 400°C (with essentially complete disappearance of benzenes) it is 0.62. In the first mentioned case, the C_6H_6/C_6D_6 ratio changes from 1.1 in the inflow to ~0.70 in the outflow. In this example, the amounts of converted C_6H_6 (770 ppm) and C_6D_6 (625 ppm) imply a ratio of 1.23. In the output, the C_6H_5Cl/C_6D_5Cl ratio of 0.78 would at first glance point at an (overall) inverse isotope effect of ~0.63. Two aspects have to be noted, however: first, if C_6H_5Cl and C_6D_5Cl are formed and released from the surface, both are subject to catalytic combustion as well, and with rates comparable with those of the benzenes (compare Section 3.4.1). Also, a kinetic isotope effect—analogous to that for the benzenes (Section 3.3) or to that for $PhCl/C_6D_5Cl$/heptane (20)—of presumably ca. 1.5 will hold. This then changes an original C_6H_5Cl/C_6D_5Cl ratio of 1.0 into ca. 0.6, after, for example, 90% conversion of the former (and 79% of the latter). The observed C_6H_5Cl/C_6D_5Cl product ratio of 0.78—when "redressed" as discussed above—becomes ~1.3. The experimental, overall isotope effect for the chlorination is now ca. 1.0–1.1. Mechanistic consequences will be dealt with in the Discussion.

4. DISCUSSION

4.1. *Sorption and Reactivity of Aromatics on Pt*

It was recently concluded that Pt—i.e., Pt(110)—can adsorb benzene to give two different forms: at high coverage in an undistorted form (as a π-complex, a η^6-species), which on heating is simply desorbed, while at low coverage a distorted dienyl-type (η^2) species can arise which is at best only partly desorbed as benzene at higher temperatures (26). While this result appears to settle a controversy in the earlier literature on the nature of adsorbed benzene, the latter form is a likely precursor for conversion—to, e.g., cyclohexene upon hydrogenation, and presumably also to oxidation products in air, at elevated temperatures. As yet it is not known if—and how—PhCl adsorption on Pt differs from benzene in this respect.

Not surprisingly, iodobenzene easily reacts by C−I bond fission already below 0°C (28) (see Fig. 8; for simplicity, only one form of sorbed C_6H_5X has been drawn). On metallic Pd, an analogous dissociative adsorption of PhCl was observed at room temperature (28); the behavior on Pt is not known.

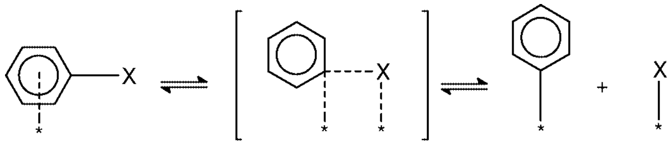

FIG. 8. An associative and dissociative chemisorption of aromatics (X = e.g., I, Cl, and H or D) (20).

Van den Brink *et al.* (19) found no isotope effect when combusting PhCl and C_6D_5Cl on a $Pt/\gamma{-}Al_2O_3$catalyst, but in the presence of heptane the reaction was much faster, while the isotope effect was ~1.5. This suggests that two different types of catalytic sites are active in the adsorption and combustion of PhCl.

With heptane present, and also reacting in part, the key step is rupture of a C−H (or D) bond, which likely results in a Pt-σ-aryl species, subsequently converted—together with metal-H (or –D)—by (adsorbed) oxygen. This allows the next reaction cycle to occur. If meanwhile metal-Cl entities arise (from the degradation of the Cl-containing σ-aryl functions) the cocombustion of the heptane can cause its removal—as HCl—which keeps the active sites intact. When PhCl is combusted alone, these sites appear to become rapidly deactivated (poisoned) by Cl. At the more elevated temperature needed, another type of site apparently comes into play, breaking the C−Cl bond. The resulting σ-aryl function may either react with surface oxygen or recombine with surface Cl—restoring the PhCl.

PhCl also contains hydrogen, and in the process of the oxidative degradation it can to some extent convert surface chlorine into HCl, to get a certain balance between surface-bound arenes, derivatives thereof, Cl, and oxygen. In the combustion of PhCl a decrease in conversion was found at higher O_2 concentrations (Fig. 2). This is (most) probably caused by an increased coverage by oxy and/or oxychloride species, diminishing the number of sites available for reaction with PhCl.

Catalytic combustion is anyway a complex affair, so rates for benzene on Pt/Al_2O_3 depend on the Pt particle size, with faster reactions on larger crystallites (29). Garetto and Apesteguia concluded that the reaction proceeds via a Langmuir–Hinshelwood mechanism, with a rapid and strong benzene adsorption and a low rate constant for oxygen adsorption compared to that for the surface reaction.

4.2. *Isotope Effects*

Competitive combustion of H/D isotope analogues is a useful tool in obtaining additional information about conversions, rate-limiting steps, and byproduct formation. Besides the kinetic isotope effect, H/D exchange between the respective species may be found. This can give additional information about the mechanism. It can come to a small isotope effect when other features such as sorption on the catalyst surface influence the reaction rates. And if the transition state is not linear, k_H/k_D may become temperature-independent (22, 30). Earlier research has shown that competitive combustion of C_6H_6 and C_6D_6 not only resulted in a high conversion rate, but also a clear-cut isotope effect, $k_H/k_D \sim 2.1$ at 150°C, was observed (20). When PhCl was cocombusted the rate is reduced and we found a k_H/k_D of 1.6.

In these reactions—and in the combustion of PhCl together with heptane, vide supra—the same type(s) of site may be involved, acting through C–H(D) bond scission. Without the presence of an—effective—hydrogen donor these sites become rapidly poisoned by Cl when chlorinated organics such as PhCl are combusted. Then, a much less active type of site can initiate oxidative degradation, by C–Cl bond activation, with a negligible H/D isotope effect as a result.

Upon reaction of C_6H_6/C_6D_6 in the presence of C_2Cl_4 (Section 3.5.1), the selectivity to C_6D_5Cl is higher than that to C_6H_5Cl. At first glance there appears to be an inverse isotope effect of ~0.6 for the chlorination reaction. Taking into account that C_6H_5Cl and C_6D_5Cl are subject to catalytic combustion as well—and with a kinetic isotope effect—we have argued in Section 3.5.1 that, basically, the formation of (free) C_6H_5Cl and C_6D_5Cl appears to occur without a significant overall H/D isotope effect.

These $PhCl_x$—byproducts of the main reaction, the oxidative degradation of the two benzenes—expectedly are formed by combination of surface-bound Cl and $C_6H_5(C_6D_5)$ (see Fig. 8 from right to left) followed by desorption of the π-complexed PhCl. This reaction will not be subject to a (primary) isotope effect. It has to compete, however, with the major reaction, oxidation of the σ-bonded C_6H_5 or C_6D_5 groups. If this reaction implies a substantial isotope effect, chlorination of C_6D_5 to C_6D_5Cl would be relatively more important than that of C_6H_5 to C_6H_5Cl, with an apparent overall inverse isotope effect as a result. Details on the key step(s) of the oxidation are not known, but two possibilities are: (i) conversion of phenyl into (sorbed) phenoxyl, e.g., by surface-bound oxygen, and (ii) abstraction of (ortho-) H or D from the σ-bonded phenyls, again by a surface oxy group, to give a benzyne-type complex. Mechanism (ii) will imply a primary isotope effect, while reaction according to (i) should be equally fast for C_6H_5 and C_6D_5. More experimental data are needed to arrive at definitive conclusions, but given our assessment of the overall isotope effect for chlorination, we prefer mechanism (i). Phenol was never observed as a byproduct, but even if it were formed as a discrete intermediate it has very little chance, if any, to survive: In the catalytic oxidation on MSW flyash (31) phenol is orders of magnitude more reactive than PhCl. And very recently, Ihm and White established that phenol—on Pt(111)—dissociates into PhO and H already at −70°C (32) (interestingly, the PhO moiety on this and other "soft" metals appears as a η^5 ligand with a "free" C=O group). At higher T there is no desorption but decomposition, to e.g., CO above ~200°C.

4.3. *Oxygen Concentration*

Finally, it is worthwhile to briefly comment on the observed effects of changing $[O_2]$ under various conditions. First, in the catalytic combustion of benzene (Section 3.2.1) the small but distinct effect—with $[O_2]$ between 8 and 14%—is difficult to explain exactly. There appears to be little change in relative coverage by oxygen, with a somewhat lower number of sites available for (chemisorption of) benzene at higher $[O_2]$.

With PhCl (Section 3.2.2) there is of course an increasing coverage by O when going from 0 to ~2 % $[O_2]$—which is altogether necessary for the oxidation of aryl groups, once formed by chemisorption—with higher rates as a result. With higher levels of oxygen, PhCl apparently has increasing difficulty in competing with O for the sites allowing its C–Cl bond activation. At the same time, (oxy)chlorination is promoted, probably with an active role of Pt (IV) (19).

5. CONCLUSIONS

The catalytic combustion of benzene on Pt/γ-alumina is a smooth reaction, proceeding well between 130 and 180°C, given the substantial kinetic H/D isotope effect, apparently via C–H bond breaking in sorbed benzene as a rate determining step. Addition of PhCl markedly retards the conversion of benzene; at the same time PhCl reacts much faster than when used alone. Apparently, Cl—freed from PhCl—blocks metal sites involved in the sorption/conversion of benzene. Chlorination is a (minor) side reaction but becomes more severe (giving $PhCl_x$) with PhCl only. Then, a slow reaction occurs, without H/D isotope effect, via C–Cl bond fission, presumably on another type of site. An increase of $[O_2]$ can lower rates somewhat further; that oxygen "functions as an antioxidant" can be understood by competition with the benzene for reactive sites.

In the cocombustion of PhCl and heptane, rates for the former are up, meaning that the latter, via its hydrogen, can remove surface Cl—as HCl—and regenerate the sites for benzene chemisorption/conversion.

Using C_2Cl_4 as a Cl source—together with C_6H_6 and C_6D_6—the (oxy)chlorination is visible from the formation of small proportions of the two chlorobenzenes; unlike the main reaction, oxidative breakdown, chlorination occurs without kinetic H/D isotope effect.

With surface-bound phenyl groups as logical intermediates, oxidation can best be interpreted via formation of phenoxyl, subject to rapid degradation. (Oxy)chlorination is likely to involve a combination of a phenyl entity with (electrophilic) chlorine, presumably at an oxidized Pt site.

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REFERENCES

1. Louw, R., and Mulder, P., *J. Environ. Sci. Health A* **25**, 555 (1990).
2. Santoro, D., and Louw, R., *Carbon* **39**, 2091 (2001).
3. Van den Brink, R. W., Krzan, M., Feijen-Jeurissen, M. M. R., Louw, R., and Mulder, P., *Appl. Catal. B* **24**, 255 (1999).
4. Van den Brink, R. W., Mulder, P., and Louw, R., *Catal. Today* **54**, 101 (1999).
5. Van den Brink, R. W., Louw, R., and Mulder, P., *Appl. Catal., B* **16**, 219 (1998).
6. Lago, R. M., Green, M. L. H., Tsang, S. C., and Odlyha, M., *Appl. Catal., B* **8**, 107 (1996).
7. Imamura, S., *Catal. Today* **11**, 547 (1992).
8. Stenger, H. G., Buzan, G. E., and Berty, J. M., *Appl. Catal., B* **2**, 117 (1993).
9. Krishnamoorthy, S., Baker, J. P., and Amiridis, M. D., *Catal. Today* **40**, 39 (1998).
10. Van den Brink, R. W., Mulder, P., Louw, R., Sinquin, G., Petit, C., and Hindermann, J.-P., *J. Catal.* **180**, 153 (1998).
11. Jang, B. H., Lee, S. S., Yeon, T. H., and Yie, J. E., *Korean J. Chem. Eng.* **15**, 516 (1998).
12. Burch, R., Crittle, D. J., and Hayes, M. J., *Catal. Today* **47**, 229 (1999).
13. Au-Yeung, J., Chen, K., Bell, A. T., and Iglesia, I., *J. Catal.* **188**, 132 (1999).
14. Burch, R., and Loader, P. K., *Appl. Catal., B* **5**, 149 (1994).
15. Spivey, J. J., *Ind. Eng. Chem. Res.* **26**, 2165 (1987).
16. Van den Brink, R. W., Louw, R., and Mulder, P., *Appl. Catal., B* **25**, 229 (2000).
17. Ozaki, A., "Isotopic Studies of Heterogeneous Catalysis." Academic Press, New York, 1977.
18. Moyes, R. B., and Wells, P. B., *Adv. Catal.* **121**, 58 (1973).
19. Van den Brink, R. W., De Jong, V., Louw, R., Maggi, P., and Mulder, P., *Catal. Lett.* **71**, 15 (2001).
20. Engel, T., and Ertl, G., *Adv. Catal.* **28**, 1 (1979).
21. Geus, J. W., Dutch Patent 259 (1967).
22. Bell, R. P., *Chem. Soc. Rev.* **3**, 513 (1974).
23. Hatje, U., Hagelstein, M., and Förster, H., *Stud. Surf. Sci. Catal.* **84**, 773 (1994).
24. Cant, N. W., Angrove, D. E., and Patterson, M. J., *Catal. Today* **44**, 93 (1998).
25. Marecot, P., Fakche, A., Kellali, B., Mabilon, G., Prigent, M., and Barbier, J., *Appl. Catal., B* **3**, 283 (1994).
26. Thomas, F. S., Chen, N. S., Ford, L. P., and Masel, R. I., *Surf. Sci.* **486**,1 (2001).
27. Yang, M. X., Xi, M., Yuan, H., Bent, B. E., Stevens, P., and White, J. M., *Surf. Sci.* **341**, 9 (1995).
28. Aarts, J. F. M., and Phelan, K. G., *Surf. Sci.* **222**, L853 (1989).
29. Garetto, T. F., and Apesteguia, C.R., *Appl. Catal. B* **32**, 83 (2001).
30. Rao, V. S., and Skinner, G. B., *J. Phys. Chem.* **92**, 2442 (1988).
31. Born, J. G. P., Louw, R., and Mulder, P., *Chemosphere* **19**, 1629 (1989).
32. Ihm, H., and White, J. M., *J. Phys. Chem. B* **104**, 6202 (2000).