

HYDRODEHALOGENATION OF SUBSTITUTED CHLOROBENZENES MEDIATED BY ACTIVATED CARBON

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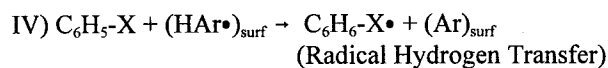
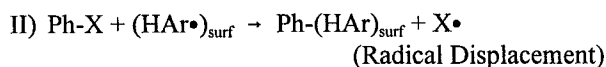
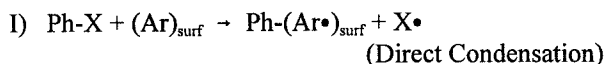
Summary

The gas phase hydrogenolysis of substituted chlorobenzenes: $Z\text{PhCl} + \text{H}_2 \rightarrow \text{PhZ} + \text{HCl}$, has been studied using flow reactors packed with Activated Carbon (AC). A marked substituent effect was observed: complete conversion was achieved at temperatures ranging from $T = 600$ K for *p*-ClPhOH to $T = 900$ K for PhCl. In the *para* series, relative rates of disappearance follow the order of adsorption heats. Binding of phenyl rings to the arene AC surface accounts for the incomplete mass balance. With ClPhOH's binding of chlorine containing groups to the AC surface also occurs.

Introduction

Currently, disposal of halogenated waste is mainly effected by incineration, which has however its drawbacks. PolyChloroDibenzo-*p*-Dioxins and PolyChloroDibenzoFurans (the well-known "dioxins") are produced during incomplete combustion. To achieve strictly regulated emission levels, high temperatures (>1500 K) are required. High cost technologies, often with additional abatement systems need to be used.

Gas phase Thermal HydroDehalogenation (THD) is an alternative: $\text{R-X} + \text{H}_2 \rightarrow \text{R-H} + \text{H-X}$, $\text{X} = \text{Cl, Br, I}$ [1, 2]. Almost complete conversion ($>99.9\%$) is obtained with (poly)chlorobenzenes and PCB's at $T = 1000$ - 1200 K. When using a flow reactor packed with AC, complete conversion of the recalcitrant organohalogen compounds is achieved at $T < 900$ K. Four major dehalogenation mechanisms have been suggested (initial, rate determining steps are pictured) [3]:



where $(\text{Ar})_{\text{surf}}$ is the (arene) AC surface. Mechanisms I) and II) envisage chemical binding of the aromatic ring to the carbon surface, and account for the observed loss in the phenyl mass balance (generally about one half of PhCl becomes PhH).

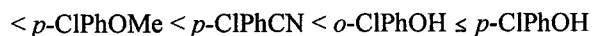
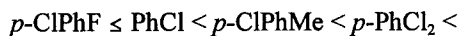
Results and Discussion

The apparatus has been described in detail elsewhere [3]. Briefly, a plug-flow quartz reactor was employed, packed in its central part with AC. Typical conditions were: inflow (mmol/h): $Z\text{PhCl} = 0.15$, PhCH_3 (diluent, inert under the applied conditions) = 1.2, $\text{H}_2 = 39$, $\text{N}_2 = 47$; carbon bed: load 1.7 g, length 6.0 cm; volume unpacked reactor: 2.95 mL; $T = 500$ - 900 K; residence time (unretained compounds) = 2-3 s. Carbon Chemviron type BPL was used; a few experiments were performed using carbon Norit type ROW 0.8 Supra and type ROX with comparable results.

In order to gain insights into the role played by substituents on the overall conversion rate, the following *para* chlorobenzenes have been tested: $Z\text{PhCl}$, $Z = \text{H, F, Cl, Me, OMe, OH, CN}$ and *o*-ClPhOH. The choice of substituents is limited by their stability under the applied conditions. A marked time dependence of the output was observed. E.g. with PhCl deactivation of the AC bed typically occurs after having processed 5-10 mmol/g AC. To avoid this, low concentrations of $Z\text{PhCl}$ were inflowed by means of dilution with toluene. Conversely, often long times were required in order to achieve stable outflows. With ClPhOH's and *p*-ClPhCN at low temperatures, a stable outflow was often not yet reached after having inflowed as much as ~ 1 mmol $Z\text{PhCl/g}$ AC. Conversion rates of these substrates are remarkably higher than that of PhCl. With PhCl the HCl outflow decreases rapidly to a low level after stopping its inflow (to $< 10\%$ of the original PhCl inflow after 30 min, $< 1\%$ after 60 min). When *p*-ClPhOH, *o*-ClPhOH, or *p*-ClPhCN are employed a substantial, persistent after-delivery of HCl is observed for several hours after stopping the organics' inflow, before reaching a low output level ($< 1\%$). Furthermore, with chlorophenols, when the temperature is rapidly increased from ≤ 600 to 900 K, a large additional

amount of HCl is produced. Soxhlet extraction showed that no significant amounts of physically adsorbed substrates were retained on the carbon bed after stopping its inflow and stripping overnight. However, when the same carbon was put back in the reactor and H₂ was inflowed while the temperature was increased from 500 K to 900 K, a large output of HCl was observed with *o*- and *p*-CIPhOH, but not with *p*-CIPhCN. Together with HCl, PhOH was the main organic outflowing compound.

Competition experiments led to the following scale of reactivity (according to the recovery of the inflowing compounds):

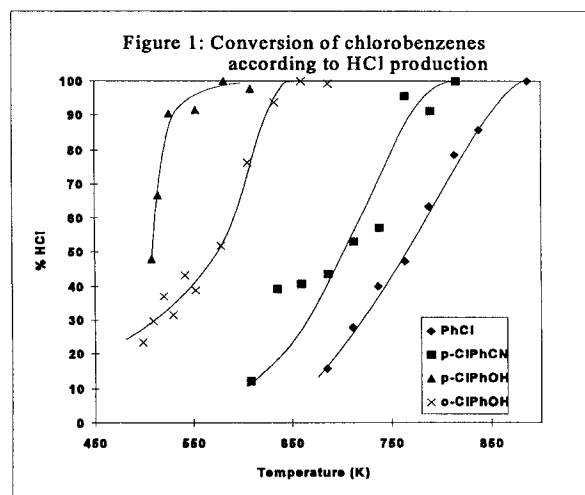


Separate experiments showed that disappearance rate and HCl yield of *m*-CIPhOH are comparable with those of its isomers. While recovery of PhCl generally matches well the HCl production, a large chlorine imbalance is found with CIPhOH's and *p*-CIPhCN at low temperatures. Their recovery is low at any temperature, unless the carbon bed is deactivated. E.g., at 572 K the recovery of *p*-CIPhCN is typically 0-8%, while HCl production at the same temperature is at best 10%; at 550 K recovery of *o*-CIPhOH is < 20%, while HCl production is at best 40%.

Conversion also occurs in inert (N₂) atmosphere. In this case, mass balances are poorer and outflow of the dechlorinated compounds relatively smaller. Deactivation occurs faster.

The observed large substituent effects appear to be related to differences in (heats of) adsorption, which in turn roughly parallel heats of vaporization. Stronger adsorption increases the residence time in the reactor and thence the overall reaction rate. However this physical model is too simple to cover all evidences and the chemistry of chlorophenols appears to be different. Conversion and HCl yields are unexpectedly high. *o*-CIPhOH has a boiling point 45 K lower than that of *p*-CIPhOH and about equal to that of *p*-PhCl₂; however its overall disappearance rate constant at 607 K is about equal to that of *p*-CIPhOH and 6-10 times larger than that of *p*-PhCl₂. Also, *p*- and *o*-CIPhOH yield novel chlorinated species which are chemically bound to the carbon surface. Dechlorination of these species becomes fast only at elevated temperatures. (This also rationalizes the scatter in HCl yield (see Fig. 1) occurring after reconditioning, with production of HCl, overnight). The nature of these species is as yet not known: C-O (Ar-O-PhCl), C-C (Ar-Ph(OH)Cl) and/or C-Cl (Ar-Cl) novel bonds may have been formed.

However, the observation of a large output of PhOH when the temperature is increased, points to the formation of ether linkages between (chloro)phenols and the arene surface.



Conclusions

Chlorinated (waste) streams including chloroaromatics can be desubstituted by means of AC mediated hydrogenolysis at relatively mild temperatures. This process seems particularly suitable for clean-up operations such as (after) treatment of gas streams with low halogen contents, remediation of contaminated soils, or as a guard bed placed after a THD reactor. Both physical and chemical sorption are important to the relative conversion rates of chlorobenzenes. Although less volatile, strongly adsorbing halogenated aromatics (including PCDD/F's if present) will hardly pass unconverted through the AC bed even at low temperatures, it is better to employ sufficiently high temperatures (≥ 900 K) in order to avoid build-up of halogenated species on the carbon bed.

Acknowledgements

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References

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