

Kinetic study of vapor phase hydrodechlorination of halons by Pd supported catalysts

S.B. Halligudi^{a,*}, Biju M. Devassay^a, A. Ghosh^b, V. Ravikumar^b

^a *Inorganic Chemistry and Catalysis Division, National Chemical Laboratory, Pune 411 008, India*

^b *Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India*

Received 7 May 2001; received in revised form 7 September 2001; accepted 11 September 2001

Abstract

Hydrodechlorination (HDC) of halons (halogenated hydrocarbons) such as *ortho*-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCIBz) were carried out under vapor phase conditions at atmospheric pressure in a fixed-bed down flow tubular glass reactor using Pd supported catalysts. HDC of ODCB with H₂ gave benzene (Bz) as the major product with chlorobenzene (ClBz) as intermediate. The effect of parameters, such as, time-on-stream, flow rates of ODCB and H₂, temperature, Pd loading and effect of supports (γ -Al₂O₃, SiO₂, carbon and MgO) were studied. HDC of TCIBz using Pd/carbon gave high selectivity for ODCB. The reaction pathways of HDC of ODCB on Pd/ γ -Al₂O₃ was established and supported by empirical kinetic modeling. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pollution; Halons; Hydrodechlorination; Pd supported catalysts

1. Introduction

Environmental pollution causing health hazards to the humans and aquatic life has increased considerably in recent years. It has been further intensified with the proliferation of industries; many poisonous chemicals have been produced and used for the production of various commercial chemicals. For example, endosulfon (pesticide) is produced in large-scale using highly toxic hexachlorocyclopentadiene (HCCP) and 2-butene-1,4-diol. HCCP causes health hazardous in working place. Similarly, many halons are used as reactants, solvents for manufacturing chemicals and also in cleaning operations such as polymeric reactors to remove polymeric materials. Clark [1] and Lapierre

et al. [2] have described that the toxic properties of halons make them very resistant to biodegradation. The link between the use of the halons and the destruction of ozone layer was first identified in the early 1970s, which culminated in the enactment of the “Montreal protocol on substances that deplete the Ozone Layer”. This initiative time tabled a worldwide phasing out of halons has been given high priority by international bodies. Option for the disposal of halons includes incineration and catalytic incineration.

Hagh and Allen [3], Rylander [4], Coq et al. [5], and Creighton et al. [6] have demonstrated in their study that catalytic hydrodechlorination (HDC) is simple, safe and more effective than incineration. Especially chlorinated aromatic compounds, where only harsh incineration conditions might presumably avoid the formation of polychlorinated benzodioxins (PCDDs) or polychlorinated benzodioxofurans (PCDFs), although might not prevent recombination to dioxins

* Corresponding author. Tel.: +91-20-5893300x2000;

fax: +91-20-5411696.

E-mail address: halligudi@cata.ncl.res.in (S.B. Halligudi).

and furans again in lowering the temperature of the fumes emitted. According to Armendia et al. [7] and others [8–16], the dehalogenation of halons is easily catalyzed by metals of group VIII of the periodic table under mild conditions. Also, Srinivas et al. [17] have used alumina supported bimetallic catalysts for selective HDC of ClBz. On the whole, the catalytic dechlorination process has been studied in liquid or vapor phase using bulk and supported noble metal catalysts. Among these, supported Pd catalysts are highly active for HDC process. Campine and Eyman [13] have used transition metal sulfide catalysts in parallel HDC of ODCB and hydrodesulfurization of methylthiophene in gas phase. Similarly, Cesteros et al. [18] have reported the effect of alumina phase and its modification on Ni/Al₂O₃ catalysts for HDC of 1,2,4-trichlorobenzene (TCIBz). Hagh et al. [3] have reported the catalytic activity of NiMO/ γ -Al₂O₃ catalysts in the HDC of ODCB.

Keeping in view of the literature on the above subject, the present paper reports the study on the vapor phase HDC of ODCB and TCIBz over Pd supported catalysts with special reference to the effect of supports on HDC of ODCB. The reaction pathways of HDC of ODCB on Pd/ γ -Al₂O₃ was established and supported by empirical kinetic modeling.

2. Experimental

2.1. Materials

Palladium chloride was procured from M/s Arora Matthey Ltd., Calcutta. Boreskov Institute of Catalysis, Novosibirsk, Russia provided γ -Al₂O₃, SiO₂, carbon (subunit) supports. M/s Loba Chimie, Mumbai, supplied (ODCB), benzene (Bz), chlorobenzene (ClBz), TCIBz, cyclohexane (CHz) of AR grade and MgO extra pure grade. Hydrogen (high purity >99.9%) used was supplied by Indian Oxygen Company (IOC), Mumbai.

2.2. Catalyst preparation

A series of Pd/ γ -Al₂O₃ catalysts were prepared by wet impregnation method. Known amount of metal precursor PdCl₂ was dissolved in minimum volume of dilute HCl and the solution was diluted to 25 ml by adding methanol. To this solution, known weight of

the support (for example γ -Al₂O₃) was added and the solution was stirred for 6 h with frequent stirring. The excess solvent was removed by placing the impregnated solution in a rotavapor maintained at 353 K. The residue thus obtained is then dried in an oven at 423 K for 12 h. This metal chloride impregnated catalyst was then calcined in the reactor at 733 K under the flow of air for 12 h. Similarly, Pd/SiO₂ and Pd/MgO catalysts were prepared and calcined before their use in the HDC experiments. Pd/C catalyst prepared as above was not calcined because active carbon impregnated with transition metal salt is susceptible to oxidation and hence used as such, in the reduction experiments to get the dispersed catalyst.

2.3. Apparatus and procedure

All the catalytic HDC reactions were carried out under atmospheric pressure in a fixed-bed down flow glass reactor (i.d. = 1.0 cm). The catalyst was placed at the center of the reactor with ceramic porcelain beads, it was then reduced at 623 K (H₂ flow = 3 l h⁻¹) for 3 h and then brought down to the reaction temperature. The reactant was fed by an ISCO-MODEL 500 D syringe pump into the reactor. The H₂ flow varied with the help of mass flow controller. The liquid products were condensed with an ice trap and were analyzed by a Shimadzu GC-15A gas chromatograph using FID and bentone packed column of length 3 m and 0.5 mm i.d. The exit flow from the reactor after condensation was passed through an alkali solution trap to adsorb HCl formed in the reaction. Surface area of the supports were determined by N₂ adsorption using Omnisorb 100 CX (Coulter, USA). These are: alumina (177.4), carbon (372), MgO (63.3) and Silica (189) sq.m/g respectively.

In a series of blank experiments, passage of the feed in a stream of H₂ in the absence of catalyst did not result in any detectable conversion. Mass diffusion contributions under the conditions of HDC reaction studied were found to be negligible, when using the approach proposed by Ruthven [19], which delivered effectiveness factors ($\eta > 0.99$). Heat transport effects can also be disregarded when applying the criteria set down by Mears [20]. In the steady-state, the material balance of the reactor evaluated by chromatography ($n_{\text{ODCB}}^0 = n_{\text{ODCB}} + n_{\text{ClBz}} + n_{\text{Bz}}$) was always better than 100 ± 5%.

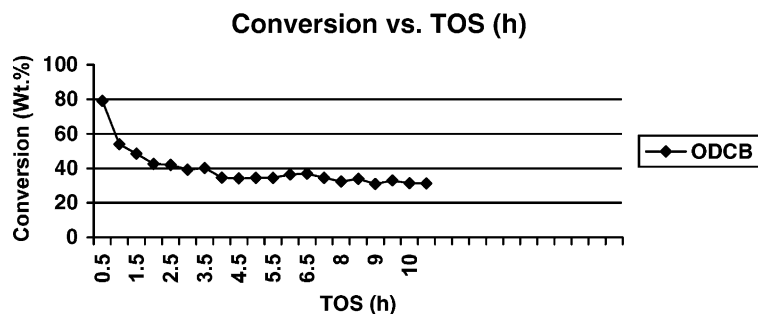


Fig. 1. Effect of time-on-stream in dechlorination of ODCB (conditions: temperature = 523 K; WHSV = 6.39 h⁻¹; catalyst = 2 g of 0.2% Pd/ γ -Al₂O₃; H₂ flow = 31 h⁻¹).

3. Results and discussion

HDC of ODCB using hydrogen catalyzed by Pd supported catalysts gave mainly two products ClBz and Bz under vapor phase conditions. Only in few cases, CHz was formed as a product of hydrogenation of Bz. Independent experiments performed on hydrogenation of Bz (under the conditions of HDC of ODCB) showed that CHz formation was negligible compared to the formation of Bz by HDC of ODCB. Hence, it was concluded that Bz was the final product of HDC of ODCB.

3.1. Time-on-stream (TOS) study

The time-on-stream behavior of HDC of ODCB is as shown in Fig. 1. It is seen from the graph that the higher conversion ODCB (>80%) was observed in the initial 0.5 h reaction time and it dropped to around 40% after 2 h. Thereafter, there was no significant change in the conversion levels and was almost steady. The

initial drop in conversion of ODCB was attributed to loss in the catalytic activity due to the inhibition of the metal surface by chlorine and the conversions do not increase further (\approx 30% conversion up to 10 h) indicating the attainment of steady-state.

3.2. Effect of Pd loading on the HDC rates

The catalysts were prepared with different Pd loading in the range (0.2–1.4 wt.%) using γ -Al₂O₃ and these were tested in HDC of ODCB. The details of the reaction conditions and the results of HDC are presented in Table 1. It was found that HDC of ODCB were steady in all the experiments from 3rd hour onwards and hence, 4th hour data has been considered for interpretation.

From the results presented in Table 1, it is seen that the conversion of ODCB increased from 32.2–55.5% with increase in Pd loading from 0.2–1.4%. While, the selectivities for all the products increased steadily, Bz (82–87%) and CHz (1.7–10.6%), where as the

Table 1
Effect of Pd loading on ODCB conversion^{a,b}

Product distribution (wt.%, 4th hour)	Pd loading (wt.%)			
	0.2	0.6	1.0	1.4
CHz	1.7 (5.2)	1.4 (3.4)	4.9 (10.0)	5.8 (10.6)
Bz	26.5 (82.2)	35.8 (87.8)	42.2 (86.7)	48.2 (86.7)
ClBz	4.0 (12.6)	3.6 (8.8)	1.5 (3.3)	1.5 (2.7)
ODCB	67.8	59.2	51.4	44.5
Conversion	32.2	40.8	48.6	55.5

^a Values in parenthesis indicate (selectivity (%)).

^b Conditions: temperature = 423 K, WHSV = 6.39 h⁻¹, weight of catalyst = 2.0 g Pd/ γ -Al₂O₃, H₂ = 31 h⁻¹ and bed height = 1.5 cm.

Table 2
Effect of temperature on conversion and selectivity^{a,b}

Product distribution (wt.%, 4th hour)	Temperature (K)					
	389	423	453	473	523	573
CHz	1.6 (13.8)	1.7 (5.2)	0.4 (1.5)	0.1 (0.3)	–	–
Bz	8.6 (74.6)	26.5 (82.3)	29.5 (82.4)	37.4 (86.0)	54.2 (92.1)	58.9 (93.7)
CIBz	1.4 (11.6)	4.0 (12.5)	5.7 (16.1)	5.9 (13.7)	4.6 (7.9)	3.9 (6.3)
ODCB	88.4	67.8	64.4	56.6	41.2	37.1
Conversion	11.6	32.2	35.6	43.4	58.8	62.9

^a Values in parenthesis indicates (selectivity (%)).

^b Conditions: WHSV = 6.39 h⁻¹, weight of catalyst = 2.0 g of 0.2% Pd/γ-Al₂O₃, H₂ = 31 h⁻¹ and bed height = 1.5 cm.

selectivity for CIBz (12.3–2.7) decreased with increase in Pd loading. Effect of Pd loading in HDC of ODCB indicated that Bz is the major product. The conversion of ODCB showed a linear dependence on Pd loading.

3.3. Effect of temperature on HDC of ODCB

Temperature is the most important parameter for any reaction. HDC of ODCB was carried out in the temperature range 389–573 K, keeping other reaction parameters constant. The catalyst containing 0.2% Pd/γ-Al₂O₃ was used for these experiments and the results are presented in Table 2. The conversion of ODCB steadily increased (11.6–62.9%) with increase in temperature (389–573 K) and is as shown in Fig. 2. ODCB conversion below its boiling point (<453 K) was found to be low (11.6%), while at temperatures near and above it's boiling point, there was a considerable increase in the conversions. It is seen that the selectivities for Bz increased, while CIBz decreased as expected with increase in temperature.

CIBz selectivities were found be the same at all temperatures since it is an intermediate product and could be easily dechlorinated under the reaction conditions.

3.4. Effect of space velocity (WHSV) and H₂/HC (ODCB) mole ratio on HDC of ODCB

Weight hourly space velocity (WHSV, h⁻¹) was varied from 6.39–13.18 h⁻¹ by adjusting the feed rates. Catalyst containing 0.2% Pd/γ-Al₂O₃ was used in these experiments and the results are presented in Table 3. It is seen that the conversion of ODCB decreased with increase in WHSV. However, there the selectivities for CIBz increased and that of Bz decreased with increase in WHSV. Similarly, the effect of H₂/HC (ODCB) mole ratio on the conversions and selectivities in HDC of ODCB was studied at 473 K and the results are presented in Table 3. Increase in H₂/HC mole ratio increased the conversions of ODCB, while the selectivities for CIBz decreased and Bz increased.

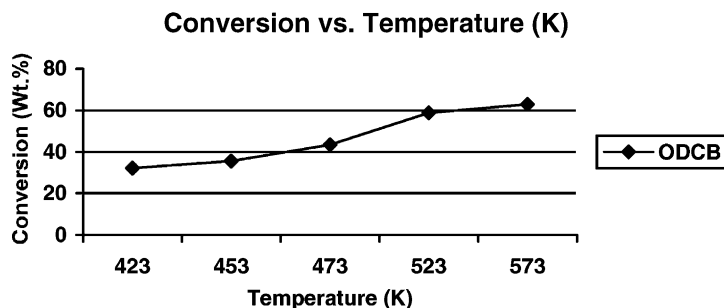


Fig. 2. Effect of temperature on the conversion of ODCB (conditions: WHSV = 6.39 h⁻¹, weight of catalyst = 2 g of 0.2% Pd/γ-Al₂O₃; H₂ = 31 h⁻¹; bed height = 1.5 cm).

Table 3
Effect of space velocity and H₂/HC mole ratio on HDC of ODCB^a

Product distribution (wt.%), 4th hour	WHSV (h ⁻¹) ^b			H ₂ /HC mole ratio ^c		
	6.39	8.48	13.18	0.8	1.48	2.5
CHz	–	–	–	–	0.1 (0.3)	1.6 (2.5)
Benzene	54.2 (92.2)	39.3 (86.7)	12.4 (70.8)	19.7 (72.6)	37.8 (86.4)	59.8 (92.7)
ClBz	4.6 (7.8)	6.1 (13.3)	5.2 (29.2)	7.4 (27.4)	5.5 (13.3)	3.1 (4.8)
ODCB	41.2	54.6	82.4	72.9	56.6	35.5
Conversion of ODCB	58.8	45.4	17.6	27.1	43.4	64.5

^a Values in parenthesis indicates (selectivity (%)).

^b Conditions: weight of catalyst = 2.0 g of 0.2% Pd/γ-Al₂O₃, H₂ = 31 h⁻¹, temperature = 523 K, bed height = 1.5 cm.

^c Conditions: weight of catalyst = 2 g of 0.2% Pd/γ-Al₂O₃, temperature = 473 K, WHSV = 6.39 h⁻¹, bed height = 1.5 cm.

Table 4
Effect of calcination on catalyst activities^{a,b}

Product distribution (wt.%), 4th hour	With calcination	Without calcination
CHz	0.1 (0.2)	0.1 (0.2)
Bz	35.4 (85.5)	23.8 (78.8)
ClBz	5.9 (14.3)	6.4 (21.0)
ODCB	58.6	69.7
Conversion	41.4	30.3

^a Values in parenthesis indicates (selectivity (%)).

^b Conditions: weight of catalyst = 2 g, temperature = 473 K, WHSV = 6.39 h⁻¹, H₂ = 31 h⁻¹, bed height = 1.5 cm.

3.5. Effect of catalyst calcination on dechlorination of ODCB

The catalysts 0.2% Pd/γ-Al₂O₃ prepared as described earlier was used in the HDC of ODCB with and without calcination. From the results presented in Table 4, it is seen that calcination had a pronounced effect on the conversion and product selectivities in HDC of ODCB. The conversion of ODCB was quite high with the calcined catalyst than the one used without calcination. This effect could be analyzed in

terms of the self-poisoning effect of chloride ions coming from the metal salt precursor. Calcination under the flow (air) condition was required to remove the chloride ions from the surface of the catalyst.

3.6. Effect of supports on HDC of ODCB

The catalyst were prepared using 0.2% Pd loading on γ-Al₂O₃, carbon, SiO₂ and MgO by following the procedure described in the previous text and tested for their activities in HDC of ODCB. The reaction conditions and the results of HDC are presented in Table 5. The surface area of the supports used are as follows:

Support	Surface area (m ² g ⁻¹)
γ-Al ₂ O ₃	177.4
Carbon (subunit)	371.9
SiO ₂	189.0
MgO	63.3

Carbon and γ-Al₂O₃ gave almost similar conversions (≈58%). Where as SiO₂ and MgO gave comparatively fewer conversions. The relative activities with

Table 5
Effect of supports on Pd catalyzed HDC of ODCB^{a,b}

Product distribution (wt.%), 4th hour	γ-Al ₂ O ₃	Carbon	SiO ₂	MgO
Bz	54.2 (92.2)	14.8 (25.6)	11.7 (39.5)	0.4 (7.1)
ClBz	4.6 (7.8)	43.1 (74.4)	17.8 (60.5)	5.3 (92.9)
ODCB	41.2	42.1	70.5	94.3
Conversion	58.8	57.9	29.5	5.7

^a Values in parenthesis indicates (selectivity (%)).

^b Conditions: catalyst = 2.0 g of 0.2% Pd on supports, WHSV = 6.39 h⁻¹, H₂ = 31 h⁻¹ and temperature = 523 K.

Table 6
Selective HDC of TCIBz by Pd/C catalyst^{a,b}

Product distribution (wt.%)	Time (h)			
	3	4	5	6
Bz	4.4 (5.5)	0.3 (1.2)	0.3 (0.9)	1.1 (2.6)
ClBz	25.3 (31.5)	3.4 (13.2)	5.1 (15.5)	9.0 (20.9)
<i>m</i> -Dichlorobenzene	6.7 (8.3)	3.7 (14.1)	4.4 (13.4)	5.2 (11.8)
<i>p</i> -Dichlorobenzene	8.8 (10.9)	4.2 (16.3)	5.2 (16.0)	6.0 (13.9)
ODCB	35.2 (43.8)	14.3 (55.2)	17.6 (54.2)	21.9 (50.7)
TCIBz	19.3	74.1	67.4	56.8
Conversion	80.7	25.9	32.6	43.2

^a Values in parenthesis indicates (selectivity (%)).

^b Conditions: catalyst = 2.0 g of 0.2% Pd/C, feed = 9.8 ml h⁻¹, H₂ = 31 h⁻¹ and temperature = 523 K.

different supports are as:



3.7. Selective HDC of TCIBz

The HDC of TCIBz was carried using Pd/carbon catalyst under optimized conditions. The results of dechlorination of TCIBz are presented in Table 6. The objectives in this study were to extend HDC reaction towards selective dechlorination of polyhalons to get the desired halons. The study on HDC of TCIBz indicated that Pd/C could be effectively used for selective dechlorination (for example: ODCB from TCIBz). At the steady-state (after 6 h), the selectivity for ODCB (50.8%) was obtained at TCIBz conversion (43.2%). Further study on this aspect is to be carried out to extend HDC reaction for selective dechlorination of polyhalons, which has applications in industry. In our recent findings, the application of HDC has been utilized in the preparation of 4,6-diaminoresorcinol [21].

3.8. Kinetic modeling studies on Pd catalyzed HDC of ODCB

Catalytic HDC of ODCB could take place in two different ways as consecutive-parallel or step-wise (consecutive) mechanism to give dechlorination products. The correlation of HDC data by consecutive-parallel scheme proposed by Juszyk et al. [22] for similar studies were found to be unsatisfactory in our case. However, a good fit was obtained using step-wise reaction with (Scheme 1) two pseudo-first-order reactions.

The rates of consumption of ODCB and the formation of ClBz and Bz can be written as

$$-d[\text{ODCB}]/d(W/F) = k_1[\text{ODCB}] \quad (1)$$

$$d[\text{ClBz}]/d(W/F) = k_1[\text{ODCB}] - k_2[\text{ClBz}] \quad (2)$$

$$d[\text{Bz}]/d(W/F) = k_2[\text{ClBz}] \quad (3)$$

where W/F = contact time (g h mol⁻¹), k_1 and k_2 are the pseudo-first-order reaction rate constants for each step. The square parentheses denotes the concentrations.

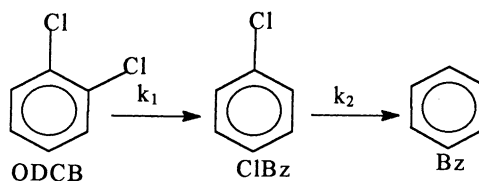
Integration of the corresponding rate equations provides the dependence of the composition on contact-time and is given as

$$a_{\text{ODCB}} = \exp[-k_1(W/F)] \quad (4)$$

$$a_{\text{ClBz}} = k_1/(k_2 - k_1) \exp[-k_1(W/F)] - \exp[-k_2(W/F)] \quad (5)$$

$$a_{\text{Bz}} = 1 - a_{\text{ODCB}} - a_{\text{ClBz}} \quad (6)$$

where, $a_{\text{ODCB}} = n_{\text{ODCB}}/n_{\text{ODCB}}^0$, $a_{\text{ClBz}} = n_{\text{ClBz}}/n_{\text{ODCB}}^0$ and $a_{\text{Bz}} = n_{\text{Bz}}/n_{\text{ODCB}}^0$ (n^0 and n are the initial



Scheme 1. Mechanism for HDC of ODCB.

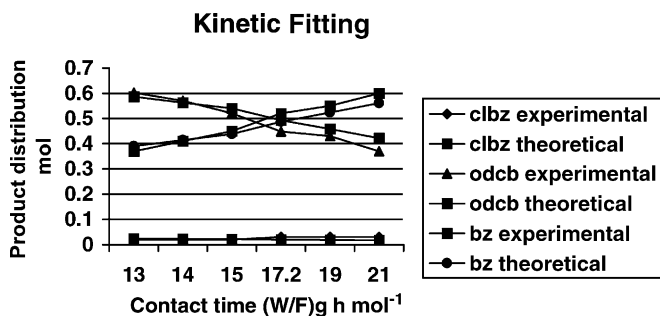


Fig. 3. Kinetic fitting of the data of HDC of ODCB.

and final number of moles)

$$\text{So } n_{\text{ODCB}}^0 = n_{\text{ODCB}} + n_{\text{ClBz}} + n_{\text{Bz}} \quad (7)$$

Kinetic fitting was carried out using Levenberg–Marquardt optimization method (Press et al. [23]) and the rate constants evolved were $k_1 = 0.0411$ and $k_2 = 1.056$. The theoretical and experimental plot is as shown in Fig. 3.

4. Conclusions

HDC of ODCB and TCIBz were studied with Pd supported catalysts and optimized reaction conditions for HDC of ODCB were Pd loading (0.2 wt.%), WHSV = 6.39 h^{-1} , H_2 flow = 31 h^{-1} and temperature = 573 K. The empirical kinetic modeling study on HDC of ODCB catalyzed by Pd/ γ - Al_2O_3 catalyst clearly demonstrated that reaction proceeds through two consecutive steps. It was also possible to extend hydrodehalogenation of polyhalogenated compounds such as TCIBz toward useful industrial applications. Hence, it is concluded that detoxification via dechlorination using H_2 gas and Pd supported catalysts is a novel and safer method for applications.

Acknowledgements

The above work has been carried out under the project entitled “Catalytic decomposition of environmentally hazardous compounds” funded by the Ministry of Environment and Forests, Government of India, New Delhi.

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