

A Kinetic Study on the Oxychlorination of Benzene

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Gas-phase benzene oxychlorination was carried out over a $\text{CuCl}_2\text{--CeCl}_3/\text{Al}_2\text{O}_3$ catalyst. A kinetic model is proposed which permits us to obtain a rate equation capable of reproducing experimental results. The presence of cerium in the catalyst increases the reaction rate and maintains the conversion level for a long time. It seems that this element facilitates copper reoxidation by making the total rate independent of the partial pressure of oxygen and stabilizes the active phase of the catalyst.

Oxychlorination is one of the most interesting ways of consuming the HCl surplus produced in conventional hydrocarbon chlorination processes.

A considerable number of kinetic studies on catalytic hydrocarbon oxychlorination are found in the paper by Allen and Clark.¹⁾ The reported data relate mainly to hydrocarbons to be oxychlorinated, reaction temperature, nature of catalyst, and whether reaction takes place in the liquid or gas phase. Most of this information relates, however, to aliphatic hydrocarbons, particularly ethylene, whereas the information about oxychlorination of aromatics in the gas phase is scarce, being restricted to the works of Solomoniv *et al.*²⁾ on toluene oxychlorination, Shutenkova and Gor'kova,³⁾ and Blanco *et al.*^{4,5)} on benzene, and Altuglu and Roberts⁶⁾ on chlorobenzene. In the case of chlorobenzene, using a $\text{CuCl}_2\text{--LiCl}/\text{Al}_2\text{O}_3$ catalyst at 200 °C,⁶⁾ the authors claimed that the Deacon reaction should not be included in the overall mechanism, and that the rate limiting step would be the formation of an activated complex compound between the hydrocarbon and adsorbed oxygen: $\text{C}_6\text{H}_5\text{ClO}^*$. Blanco *et al.* have published reports of studies on benzene oxychlorination using $\text{CuCl}_2/\text{alumina}$ ^{7,8)} and $\text{CuCl}_2\text{--KCl}/\text{alumina}$.^{4,5)} In these studies they have pointed out the existence of an interaction between copper cations and OH groups of the support.

Lately they have developed a series of catalysts containing copper and cerium chlorides on alumina that exhibit greater activity than copper chloride or mixtures of copper and alkali metal chlorides.

In this communication, the behaviour of these $\text{CuCl}_2\text{--CeCl}_3/\text{Al}_2\text{O}_3$ catalysts has been studied for the oxychlorination of benzene, and the results are compared with kinetic data previously reported.

Experimental

Apparatus. The experiments were carried out at atmospheric pressure in a conventional fixed-bed flow catalytic reactor described elsewhere.⁹⁾ The exit gases from the reactor pass through a condenser where the liquid products are collected, and then through a water adsorption column to remove unreacted HCl. The chlorinated products in the organic condensate were analyzed by GLC in a column (6.5 mm × 4.2 m) of SE. 30 Silicone rubber on Chromosorb P (60–80 mesh). Complete balance of C, H₂, and Cl₂ was confirmed for each experiment.

Catalyst. The catalyst used in this work was prepared

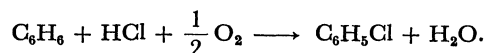
by impregnation of gamma- Al_2O_3 (EPA, high purity, containing $\text{Fe}_2\text{O}_3 \leq 0.05\%$; $\text{SiO}_2 \leq 0.5\%$; $\text{Na}_2\text{O} \leq 0.01\%$; $\text{K}_2\text{O} \leq 0.05\%$; $\text{LOI} = 7.0\%$) with aqueous solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Carlo Erba) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (BDH), and drying at 110 °C for 2 h. The alumina support was previously treated at 400 °C in air for 12 h.

The catalyst obtained has surface area 152 m²/g, pore volume 0.351 cm³/g, average pore radius 55 Å, and metal contents 0.42×10^{-3} g-atom Cu/g cat. and 0.40×10^{-3} g-atom Ce/g cat., as determined by atomic absorption spectrophotometry, equivalent to about 2.7 wt% Cu and 6.1 wt% Ce. The E.D.A.X. analysis showed that both elements are totally mixed and uniformly distributed throughout the support.

Results and Discussion

Exploratory runs were initially performed in order to define the range of experimental conditions in which the rate is not limited by mass transfer. A test carried out with the reactor packed with support alone gave no detectable conversion.

The effect of reaction temperature and contact time on rate and selectivity was studied with a stoichiometric feed mixture according to the equation



The operation conditions employed were: reaction temperature, T , 230–300 °C; pressure, P , 700 ± 10 mmHg (1 mmHg = 133.322 Pa); weight of catalyst, W , 1–12 g; catalyst size, 1–2 mm; benzene feed, F_b , $(1.125\text{--}2.25) \times 10^{-3}$ mol min⁻¹; feed composition, $\text{C}_6\text{H}_6 : \text{HCl} : \text{O}_2 : \text{N}_2 = 1 : 1 : 0.5 : 1.9$ molar ratio; and Reynold Number, 20–40.

The catalyst was dispersed over 2–3 mm carborundum particles in order to obtain a bed of 25 cm. In this way the actual reaction temperature was only 1 °C off the desired value over more than 90% of the catalyst bed.

The results obtained are summarized in Table 1, where total benzene conversion (mol of benzene reacted per 100 mol of benzene fed) and product selectivities (mol of each product formed per 100 mol of benzene reacted) are shown.

These results clearly indicate that the maximum benzene conversion to be attained with the stoichiometric feed ratio is about 70%, since part of the starting HCl and O₂ is consumed in the production of higher chlorinated compounds (dichloro- and trichlorobenzene); to avoid this limitation, a series of experiments was carried out at 270 °C with amounts of HCl and O₂

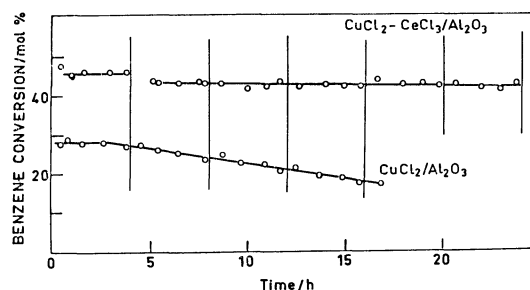
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TABLE 1. EFFECT OF REACTION TEMPERATURE AND CONTACT TIME ON BENZENE CONVERSION AND SELECTIVITY

Temp °C	Pressure total atm	$W/F_b^a)$ g min mol ⁻¹ (Benzene)	Conversion mol %	Selectivity/mol%			
				C ₆ H ₅ Cl	<i>p</i> -C ₆ H ₄ Cl ₂	<i>o</i> -C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₃
300	0.929	444	25.1	83.4	11.8	4.7	0.2
300	0.922	889	42.9	79.3	14.6	5.8	0.4
300	0.921	1778	57.9	71.9	19.7	7.7	0.6
300	0.932	3556	64.1	69.4	21.5	8.4	0.8
300	0.929	7111	66.4	65.9	24.1	9.0	1.0
270	0.928	444	11.5	92.3	5.6	2.1	0.0
270	0.925	889	22.3	87.7	8.3	4.0	0.0
270	0.929	1333	32.0	87.1	9.4	3.4	0.0
270	0.930	1778	40.7	81.5	11.7	6.5	0.2
270	0.930	3556	56.7	74.4	19.0	6.1	0.5
270	0.922	5333	65.1	69.9	22.1	7.6	0.4
270	0.926	7111	69.1	66.3	24.2	8.7	0.8
250	0.925	889	12.2	94.2	4.3	1.5	0.0
250	0.933	1778	17.2	92.8	5.2	1.9	0.0
250	0.930	3556	38.1	87.1	9.6	3.4	0.0
250	0.932	5333	47.8	79.5	15.1	5.2	0.2
250	0.922	10667	57.1	74.6	18.5	6.5	0.3
230	0.934	3556	14.7	93.9	4.5	1.5	0.0
230	0.928	5333	19.9	93.0	5.1	1.9	0.0
230	0.931	8889	27.2	89.8	7.6	2.5	0.0

a) Feed molar ratio is stoichiometric to the formation of C₆H₅Cl.TABLE 2. EFFECT OF CONTACT TIME ON BENZENE CONVERSION AND SELECTIVITY^{a)}

Pressure total atm	W/F_b g min mol ⁻¹ (Benzene)	Conversion mol%	Selectivity/mol%			
			C ₆ H ₅ Cl	<i>p</i> -C ₆ H ₄ Cl ₂	<i>o</i> -C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₃
0.930	444	11.2	91.5	6.2	2.3	0.0
0.928	889	26.2	81.6	12.1	5.8	0.2
0.934	1778	34.8	82.8	12.3	4.6	0.3
0.932	3556	59.4	69.7	21.8	7.8	0.7
0.933	7111	78.3	54.1	32.4	11.7	1.8
0.934 ^{b)}	254	4.9	—	72.4	26.8	0.8
0.930 ^{b)}	507	10.2	—	72.3	26.6	1.0
0.930 ^{b)}	4064	56.8	—	71.6	24.0	4.4

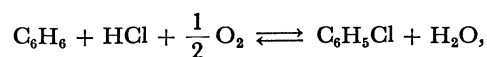
a) Feed molar ratio is stoichiometric to the formation of dichlorobenzene. Temperature of reaction is 270±1 °C. b) Experiments carried out with C₆H₅Cl in the feed instead of benzene.Fig. 1. Accelerated life test carried out at 330±1 °C with $W/F_b=444$ g min mol⁻¹ (benzene) for CuCl₂-CeCl₃/Al₂O₃ and CuCl₂/Al₂O₃ catalysts.

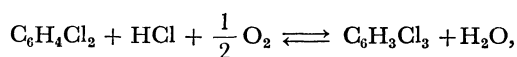
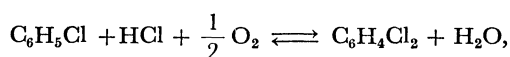
in the feed corresponding to the stoichiometric ratio for the formation of dichlorobenzene. The results are shown in Table 2, together with another series of experiments in which chlorobenzene was the starting

material and HCl and O₂ were fed in stoichiometric ratio to produce dichlorobenzene.

Finally, the influence of operation time on catalyst activity was examined by performing an accelerated life test at 330 °C, with the conditions of W/F_b 444 g min (mol benzene)⁻¹, atmospheric pressure, and feed molar ratio C₆H₆ : HCl : O₂ : N₂=1 : 1 : 0.5 : 1.9. The system was put in operation for 4 h a day during 6 d. The results of conversion *vs.* time on stream are plotted in Fig. 1. The upper curve corresponds to the catalyst studied in this work while the lower one corresponds to a catalyst containing only CuCl₂ on Al₂O₃, which was prepared by substituting the CeCl₃ by the equivalent amount of CuCl₂.

For the analysis of the experimental results the following reaction scheme is proposed:





in which no distinction is made between the *o*- and *p*-dichlorobenzene, as far as their rates of formation and further reaction is concerned. This simplifying assumption can be reasonably introduced on the basis of the experimental data that showed a constant molar ratio of both isomers at all conversion levels of para/ortho = 2.7 ± 0.2 .

According to the above scheme, different rate equations were tested by considering several orders of reaction for the various compounds taking part in the process, and different rate controlling steps. A mathematical fitting of the experimental data to the various equations was carried out through analytical integration of the different sets of rate equations by using a 4th order Runge-Kutta method, and the values of the parameters were estimated through nonlinear regression analysis by using also duplicate runs.

The optimized parameter was the variance of correlation defined by

$$\sigma^2 = \frac{\sum_{i=1}^N \sum_{j=1}^{N'} (x_{ij}(\text{exp}) - x_{ij}(\text{theor}))^2}{N \times N' - N''},$$

where N is the number of points, N' the number of yields by point, and N'' the number of parameters to be determined.

The experimental error resulting from repeated experiments was estimated by

$$\epsilon = \frac{\sum_{i=1}^N \sum_{j=1}^{N'} \sum_{k=1}^{N''} (x_{ijk}(\text{exp}) - x_{ijk}(\text{average}))^2}{N' \times N - N'''} = 0.24 \times 10^{-3},$$

where N''' is the number of average values.

The best fit was obtained with the following set of Langmuir-Hinshelwood type equations:

$$\text{Benzene disappearance: } -\frac{dx}{d\left(\frac{W}{F_b}\right)} = \frac{k_1 P_{\text{C}_6\text{H}_6}}{(1 + K_A P_{\text{H}_2\text{O}})^2},$$

Chlorobenzene formation:

$$\frac{dx_1}{d\left(\frac{W}{F_b}\right)} = \frac{k_1 P_{\text{C}_6\text{H}_6}}{(1 + K_A P_{\text{H}_2\text{O}})^2} - \frac{k_2 P_{\text{C}_6\text{H}_5\text{Cl}}}{(1 + K_A P_{\text{H}_2\text{O}})^2},$$

Dichlorobenzene formation:

$$\frac{dx_2}{d\left(\frac{W}{F_b}\right)} = \frac{k_2 P_{\text{C}_6\text{H}_5\text{Cl}}}{(1 + K_A P_{\text{H}_2\text{O}})^2} - \frac{k_3 P_{\text{C}_6\text{H}_4\text{Cl}_2}}{(1 + K_A P_{\text{H}_2\text{O}})^2},$$

Trichlorobenzene formation:

$$\frac{dx_3}{d\left(\frac{W}{F_b}\right)} = \frac{k_3 P_{\text{C}_6\text{H}_4\text{Cl}_2}}{(1 + K_A P_{\text{H}_2\text{O}})^2}.$$

Table 3 shows the values of the different kinetic parameters obtained at various temperatures. From these values a similar apparent activation energy is obtained for the oxychlorination of benzene (19.5 ± 0.3 kcal/mol) and chlorobenzene (20.1 ± 0.3 kcal/mol), the

TABLE 3. RATE CONSTANTS AND VARIANCE OF THE CORRELATION OBTAINED AT DIFFERENT TEMPERATURES

Temp °C	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_3 \times 10^5$	K_A	σ^2
230	2.753	1.802	—	8.142	2.078×10^{-6}
250	7.028	4.344	—	3.696	2.223×10^{-4}
270	13.97	9.203	9.621	1.422	2.228×10^{-4}
300	30.42	20.87	20.51	0.9466	2.205×10^{-4}

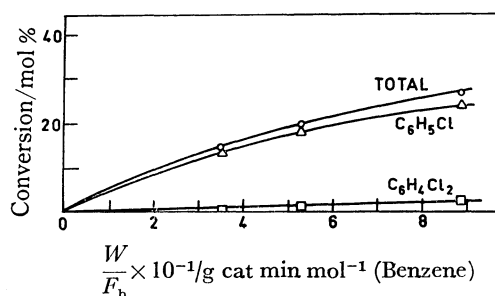


Fig. 2. Experimental results and calculated curves based on the proposed equations at 230 ± 1 °C: Δ , conversion of benzene; Δ , $\text{C}_6\text{H}_5\text{Cl}$ formation; $\square$, $\text{C}_6\text{H}_4\text{Cl}_2$ formation.

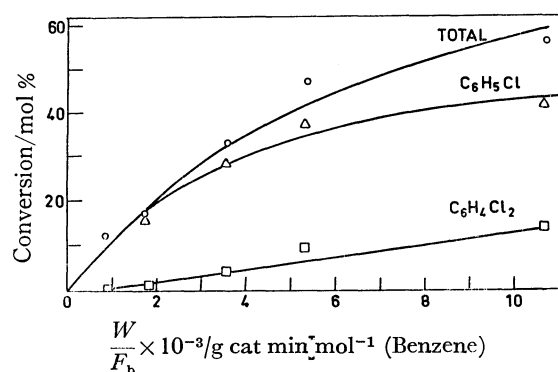


Fig. 3. The same title with Fig. 2 except that the temperature is 250 ± 1 °C.

small difference being probably due to the "deactivation" of the aromatic ring by the presence of the chlorine atom.

The variation of K_A with temperature can be related to the heat of adsorption of water on the surface of catalyst, which has a negative effect on the rates, possibly by partially blocking the active sites.

The ratio between the correlation variance and the experimental error was lower than the Fisher parameter¹⁰ $F_{(32,21)}$ for 90% = 1.71.

The experimental conversion data obtained at different temperatures are compared in Figs. 2–5 with those calculated by using the proposed equations (continuous lines). These equations reproduce the experimental values satisfactorily the data obtained at 300 °C, where the consumption of HCl and O_2 produced a dramatic decrease in their partial pressures. The dotted line corresponds to the 90% consumption of HCl and O_2 . Under these conditions the catalyst may also undergo a change in its active phase composition.

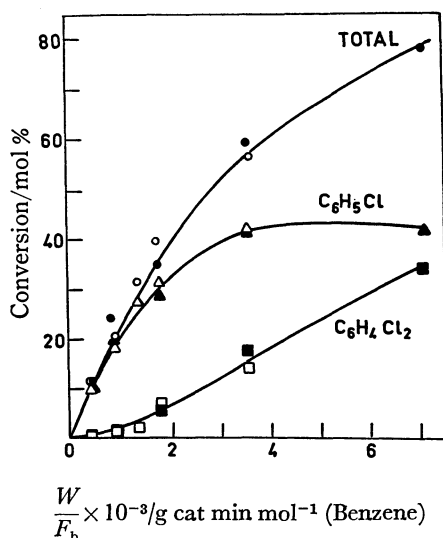


Fig. 4. The same title with Fig. 2 except that the temperature is $270 \pm 1^\circ\text{C}$. The full points correspond to experiments with a feed molar ratio stoichiometric to the $\text{C}_6\text{H}_4\text{Cl}_2$ formation.

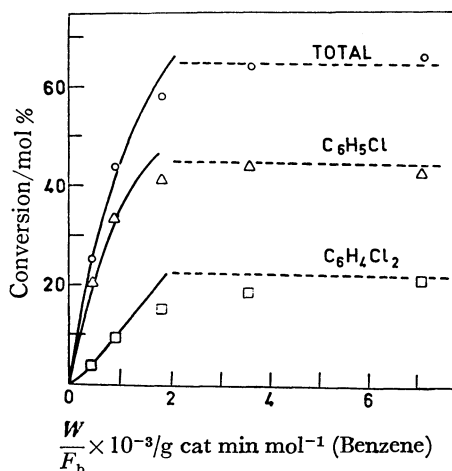


Fig. 5. The same title with Fig. 2 except that the temperature is $300 \pm 1^\circ\text{C}$. The dotted line corresponds to 90% and O_2 consumption.

The fitness of the experimental data, obtained by replacing benzene with chlorobenzene as feedstock (Table 2), appears in Fig. 6. The use of the parameter values shown in Table 3 gives calculated conversions slightly smaller than the experimental ones. This difference may be due to an effect caused by the benzene adsorption which was neglected in the proposed equations. In any cases, the deviations fell within the experimental error.

According to the proposed equations, the process may be considered independent of the partial pressures of oxygen and hydrogen chloride, the reaction rate being only a function of the partial pressures of the hydrocarbon and water.

In Table 4, the kinetic equations published in previous papers are listed together with the one proposed in this study. As can be seen, when CuCl_2 and CuCl_2 -alkali chloride supported catalysts are used, the reaction rate depends on the partial pressure of oxygen, but in the

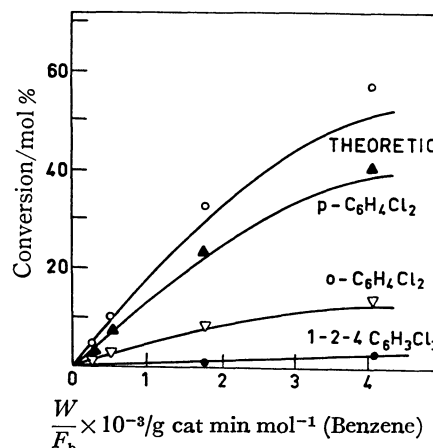


Fig. 6. Experimental results obtained for the chlorobenzene oxychlorination and calculated curves based on the proposed equations at $270 \pm 1^\circ\text{C}$: $\circ$, conversion of $\text{C}_6\text{H}_5\text{Cl}$; $\triangle$, $p\text{-C}_6\text{H}_4\text{Cl}_2$ formation; ∇ , $o\text{-C}_6\text{H}_4\text{Cl}_2$ formation; $\bullet$, 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$ formation.

TABLE 4. RATE EQUATIONS OBTAINED FOR THE OXYCHLORINATION OF AROMATIC HYDROCARBONS WITH DIFFERENT CATALYSTS

Reference	Catalyst	Rate equation
11	$\text{CuCl}_2/\text{Al}_2\text{O}_3$	$r = \frac{k_1 P_{\text{HC}} \cdot k_2 P_{\text{O}_2}^{1/2}}{k_1 P_{\text{HC}} + k_2 P_{\text{O}_2}^{1/2}}$
5	$\text{CuCl}_2\text{-KCl}/\text{Al}_2\text{O}_3$	$r = k P_{\text{HC}} \cdot P_{\text{O}_2}^{1/2}$
6	$\text{CuCl}_2\text{-LiCl}/\text{Al}_2\text{O}_3$	$r = \frac{k_1 P_{\text{HC}} \cdot P_{\text{O}_2}^{1/2}}{(1 + k_2 P_{\text{HC}} + k_3 P_{\text{O}_2}^{1/2})^2}$
This study	$\text{CuCl}_2\text{-CeCl}_3/\text{Al}_2\text{O}_3$	$r = \frac{k_1 P_{\text{HC}}}{(1 + K_A P_{\text{H}_2\text{O}})^2}$

case of $\text{CuCl}_2\text{-CeCl}_3/\text{Al}_2\text{O}_3$ this relation is no longer applicable.

The presence of cerium seems to facilitate the copper reoxidation step by making the overall rate higher and also independent of the partial pressure of oxygen. Moreover, the life test results indicate that the cerium in these catalysts not only increases the reaction rate but also maintains the conversion level for a longer time. This effect may be due to the formation of Cu and Ce complex compounds on the alumina surface,¹²⁾ which are more stable and therefore less likely to undergo the decomposition to CuCl_2 , a phenomenon considered to be the main reason for the deactivation of these catalysts.⁸⁾

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