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Conversion of Chlorobenzene over Palladium and Rhodium Catalysts of Widely Varying Dispersion

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The kinetics of hydrodechlorination of chlorobenzene have been investigated over Pd/Al_2O_3 and Rh/Al_2O_3 catalysts of varying dispersion. A reaction scheme is proposed which is formally analogous to the Mars–van Krevelen mechanism for the oxidation of hydrocarbons. Chlorobenzene interacts with the surface to form a surface chloride and benzene; hydrogen restores a H-covered surface and HCl competes with the reactant for the chlorination step. The kinetic equation fits well with the experimental data and the rate constants of these three different steps may then be obtained. An influence of particle size appears on the different steps, and particularly on the toxicity of chlorine which decreases with the size of the metallic particle. The lower reactivity of rhodium catalysts is attributed to a greater inhibition of the surface by chlorine. On Rh/Al_2O_3 the selectivity benzene/chlorocyclohexane depends on the dispersion of the metal. The formation of chlorocyclohexane is also closely related to the surface coverage in hydrogen under the conditions of reaction. The benzene produced by the main reaction can be hydrogenated to cyclohexane. Compared with the reaction of pure benzene, this reaction shows a promoter effect of chlorine in the case of Pd catalysts and an inhibition effect in the case of rhodium. This effect can be explained by the known modifications of the metal by the adsorbed chlorine species.

INTRODUCTION

The selective cleavage of C—S, C—O, C—Cl, and C—N bonds is an important process in the manufacture of fine chemicals. The removal of these heteroatoms can be achieved over classical mixed sulfide catalysts in rather drastic conditions (*1a*). Much milder conditions can be used with noble metal catalysts (*1b*), especially with rhodium and palladium, which also yield high selectivities. The present work is devoted to hydrodechlorination: chlorobenzene was taken as a simple model reactant for this reaction with the purpose to investigate the mechanism and the influence of structure sensitivity on the catalytic properties.

The mechanism of C—Cl hydrogenolysis is still controversial (*2–5*). The reaction has been described either as an interaction between two adsorbed species (*5*) or as the interaction between a gaseous molecule and a surface compound (*3, 4*). Self-poisoning by the HCl produced in the reaction is important (2, 6) and complicates the kinetics. This point has not been considered in detail in the previous studies, but will be emphasized here. A second point of interest is the structure sensitivity of the reaction, which was pointed out in a previous note in the case of rhodium catalysts (*6*). Several results support this hypothesis on platinum and palladium catalysts: the selectivity of dechlorination depends on sulfur poisoning (*7*), on alloying (*8*), and on the support (*4*), thus suggesting that the reaction proceeds at specific surface sites.

However, much of this previous work was carried out in the liquid phase, using complex molecules. Our purpose has been to check ideas using a simple model compound in the gas phase to avoid the competitive adsorption of the solvent.

We present here the results obtained in the conversion of chlorobenzene on a series

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of supported rhodium and palladium catalysts which have been previously used for the reaction of hydrocarbons (*9, 10*).

EXPERIMENTAL

Catalysts. The preparation and characterization of Rh/Al_2O_3 and Pd/Al_2O_3 have been described in detail previously (*9, 10*). The γ-alumina carriers used were samples supplied by Rhône-Poulenc (202 $m^2\ g^{-1}$), Degussa (180 $m^2\ g^{-1}$), and a "homemade" sample (350 $m^2\ g^{-1}$). The carrier was calcined for 4 h at 500°C before use, then equilibrated at $pH \simeq 2$ with a solution of HCl and finally dried overnight at 120°C. The size range of the alumina particles was 80–120 μm. Rhodium was introduced either by impregnation with $(Rh(NH_3)_5)Cl_2$ or by ion exchange with an aqueous solution of $RhCl_3 \cdot 3H_2O$ in HCl at pH ~ 2. Palladium was introduced either by ion exchange with $PdCl_2$ in HCl at pH ~2 or by impregnation with $PdCl_2$ in ammonia. Some palladium samples were also prepared from an organometallic precursor, Pd acetylacetonate $(Pd(C_5H_7O_2)_2)$ in a benzene medium, according to the procedure described by Boitiaux *et al.* (*11*).

As expected, the reduction at low temperature of an ion-exchanged sample which has been previously calcined at 500°C yielded a well-dispersed catalyst. The degree of sintering increases when the reduction temperature and/or the partial pressure of water increases.

The dispersion of the metallic phase was determined by volumetry using a conventional apparatus and H_2 adsorption in the 0–10 Torr pressure range; in line with previous studies (*9, 10*) a stoichiometry H/metal = 1 was assumed. Some characteristic properties of these catalysts are summarized in Table 1. Two catalysts, CGF19A and CGF11A, have been examined by transmission electron microscopy (TEM) before and after the reaction. For both samples the average particle size was not changed; however, a narrowing of the particle size distribution seems to be present after reaction.

Catalytic measurements. A conventional flow reactor was used in differential mode. The reactants were chlorobenzene (CBz) from Carlo Erba (RPE purity grade) and hydrogen (purity > 99%). The purity of CBz was better than 99.99% since no impurity

TABLE 1

Catalyst Characteristics

Catalysts				Thermal treatment			Dispersion (%)
Name	Metal loading (metal %)	Support[a]	Precursor[b]	Calcination	Reduction temperature (K)	Duration (h)	
FU134	Pd1.2	Deg.	PC	No	673	—	3
CGF11A	Pd0.8	R.P.	PC	Yes	473	1	5
FU135	Pd1.2	Deg.	PC	No	423	—	19
CGDA	Pd2	R.P.	PC	Yes	673	4	47
CGF20A	Pd0.34	R.P.	PAC	Yes	573	2	64
CGF11'A	Pd0.55	R.P.	PC	Yes	433	2	65
CGF19A	Pd0.25	R.P.	PAC	Yes	573	3	72
FU175	Pd1	I.R.C.	PC	Yes	473	—	80
CGF15	Rh0.7	R.P.	RA	No	1123	40	14
RAF	Rh1.8	R.P.	RC	No	773	8	27
CGF3A	Rh1	R.P.	RC	No	623	15	45
CGF16A	Rh0.25	R.P.	RC	Yes	773	4	100

[a] Deg., Degussa; R.P., Rhône-Poulenc; I.R.C., home-made.

[b] PC, palladium chloride; PAC, palladium acetylacetonate; RA, rhodium amine; RC, rhodium chloride.

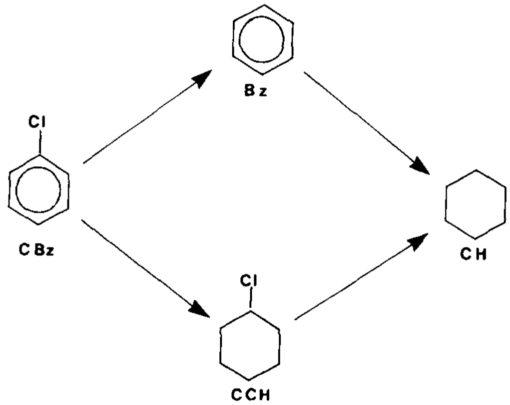
could be detected. In some experiments H_2 was diluted with helium of the same purity grade. Hydrogen was saturated with the vapor pressure of CBz at various temperatures in order to obtain a CBz pressure ranging from 0.3 to 63.3 Torr. In order to avoid condensation of CBz in the feed lines, the connecting tubes were heated, and all the valves (control and sampling) were located in a "hot-box" maintained at 80°C. Products and reactants were analyzed by on-stream gas chromatography using a column (2 m × 1/8 in.) packed with 10% Carbowax 20 M on Gas-Chrom Q (120–140 Mesh). The standard reaction temperature was 353 K. Under these conditions, the reaction yields essentially benzene (Bz), chlorocyclohexane (CCH), and cyclohexane (CH) by a secondary reaction.

Depending on the reactivity of the solid, the catalyst amount for the reaction ranged from 0.02 to 0.1 g, and the H_2 flow rate from 0.33 to 20 ml · s^{-1}.

Whatever the reaction conditions, diffusional limitations can be ruled out since, using the criterion of Weisz, Φ values were maintained much lower than 1.

RESULTS

In the course of CBz conversion three products were observed, which correspond to the reaction scheme:



The CCH selectivity was very low whatever the reaction conditions, between 1 and 7% on Rh/Al_2O_3 and less than 0.1% on Pd/Al_2O_3. Chlorine removal from chlorocycloalkane is very difficult and occurs at a much lower rate than that of CBz (*1*); moreover, the ratio (CBz + Bz)/CCH does not change in a very large range of conversion. Thus we have accounted (CH + Bz) for the total Bz formation.

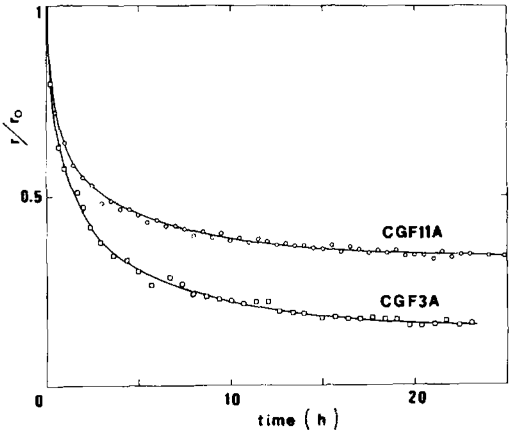


FIG. 1. Variation of the relative activity as a function of time on stream on Pd/Al_2O_3 CGF11A (initial conversion α_T = 48.2%) and Rh/Al_2O_3 CGF3A (initial conversion α_T = 2.26%).

In the conditions of the reaction, all the samples suffer a "self-poisoning" which is due to the interaction between the metallic phase and HCl produced in the reaction. With a partial pressure of 24.6 Torr a constant activity is reached after 24 h on stream. The constancy of the surface properties is satisfying for the kinetic study, since at the end of the experiments (after about 24 h) only a change of less than 10% of the initial activity is noticed. Figure 1 shows the time history of the deactivation process of two catalysts. We can see that the Pd sample suffers a deactivation of the same order of magnitude as Rh despite an HCl pressure 100 times greater. At the steady state a reversible "self-inhibition" of the metallic surface by HCl occurs: the rate decreases when the conversion increases (Fig. 2).

This initial decay seems sensitive to the presence of water. By lowering the water vapor concentration in the gas phase the level of irreversible deactivation decreases.

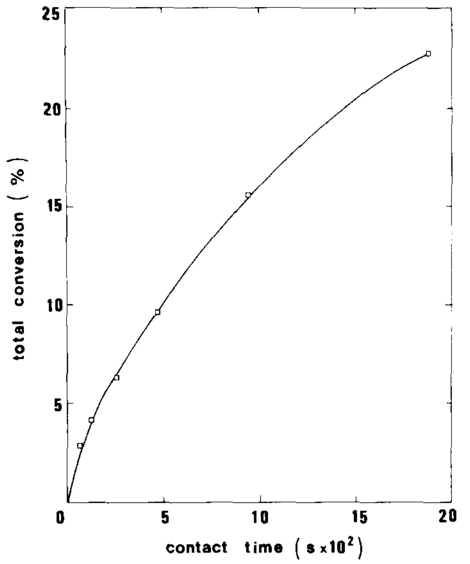


FIG. 2. Total conversion as a function of the contact time for Pd/Al_2O_3 CGF11A. T = 353 K; P_{CBz} = 24.6 Torr.

TABLE 3

Dependence of Chlorobenzene Conversion Rate on the Pressure of Chlorobenzene and Hydrogen Chloride for Rh/Al_2O_3 (CGF3A); T = 353 K

P_{CBz} (Torr)	P_{HCl} (Torr)	P_{H_2} (Torr)	Reaction rate (mol · s^{-1} · g_{cat}^{-1} × 10^8)
24.6	0.093	735	6.80
24.6	0.332	735	4.55
24.6	0.167	735	6.12
24.6	0.044	735	10.30
24.6	1.720	733	3.35
12.3	0.129	747	9.15
6.15	0.060	754	8.75
3.1	0.030	757	9.60
2.46	0.066	757	5.05
2.46	0.935	756	1.65
2.46	0.216	757	2.93
2.46	0.113	757	4.11
2.46	0.032	757	7.22
1.23	0.070	759	5.13
0.62	0.037	759	5.40
0.31	0.021	760	6.0

This is interpreted by the dissociated hydrochloric acid which strongly interacts with noble metal particles. However, the steady state activity appears little dependent on this water content.

Tables 2 and 3 present the kinetic data obtained on Pd and Rh samples, FU134 and CGF3A, respectively. We can see the very strong self-inhibition effect of HCl, since on Pd/Al_2O_3 the rate decreases sharply when the HCl pressure increases from 0.16 to 3 Torr. Moreover, at high CBz pressure the rate does not change. All samples exhibit a similar behavior.

The reactivity of Pd is 100 times larger than that of Rh. This observation is in agreement with the fact that Pd is the most efficient hydrodechlorination metal (*1*).

The influence of hydrogen pressure is shown in Table 4 at two different CBz pressures on Pd/Al_2O_3 (FU134 sample).

Apparent activation energies were deter-

TABLE 2

Dependence of Chlorobenzene Conversion Rate on the Chlorobenzene and Hydrogen Chloride Pressures on Pd/Al_2O_3 (CGF11A); T = 353 K

P_{CBz} (Torr)	Reaction rate (mol · s^{-1} · g_{cat}^{-1} × 10^6) P_{HCl} (Torr)						
	0.16	0.32	0.63	0.79	1.27	1.90	3.16
63.1	7.98	7.95	7.95	7.65	7.57	7.12	6.69
24.6	8.00	7.97	7.25	6.71	5.23	4.16	3.19
8.42	7.95	6.02	4.31	3.68	2.41	1.76	1.21
2.46	3.62	2.75	1.33	1.07	0.68	—	—
1.00	1.89	0.89	0.39	—	—	—	—

Note. P_{H_2} = 760 − P_{CBz} (in Torr).

TABLE 4

Dependence of Chlorobenzene Conversion Rate on the Hydrogen and Chlorobenzene Pressure on Pd/Al_2O_3 (CGF11A)

P_{CBz} (Torr)	Reaction rate (mol · s^{-1} · g_{cat}^{-1} × 10^6) P_{H_2} (atm)					
	1	0.75	0.5	0.25	0.067	0.017
63.1[a]	7.95	—	5.75	—	1.42	0.57
0.55[b]	2.00	1.40	1.13	0.87	0.70	0.41

[a] P_{HCl} = 0.31 Torr.

[b] P_{HCl} = 0.066 Torr.

TABLE 5

Apparent Activation Energies[a]

Sample	Metal	Dispersion (%)	E_A (kcal mol^{-1})
FU134	Pd	3	21.5
CGF11A	Pd	5	18.9
CGF20A	Pd	64	25.9
CGF11'A	Pd	65	32
CGF19A	Pd	72	29.5
RAF	Rh	27	23
CGF3A	Rh	45	18.1
CGF16A	Rh	100	20

[a] Determined in the range 333–373 K at 5% overall conversion.

mined on different samples in the range 333–373 K; they are quoted in Table 5.

DISCUSSION

An important feature is the role played by HCl produced in the reaction. Two phenomena are present:

(1) During the first hours where CBz is processed, we observed a deactivation of the sample (Fig. 1), due to interaction between metal and HCl. These chlorine species, strongly held to the surface, cannot be removed by a simple treatment under hydrogen, even at elevated temperature. An oxidizing treatment followed by a reduction step is necessary to restore part of the initial activity. The same behavior was observed previously for similar catalysts after sulfur poisoning (*13*). This irreversible initial deactivation may be explained by the formation of a stable surface chloride. The poisoning effect of these chlorine species can be represented by an initial toxicity *t*, defined following Maurel and Barbier (*14*) as the number of surface metal atoms deactivated by one molecule of poison, at low coverage. In practice, *t* corresponds to the initial slope of the deactivation curve, where the relative activity r/r_0 is plotted against the total amount of HCl produced by the reaction. Table 6 presents the values of this toxicity for several catalysts, with the residual relative activities retained at the steady state and the pressure of HCl corresponding to this steady state. Rhodium appears to be much more sensitive than palladium to chlorine poisoning: one Rh atom is poisoned when 20 HCl molecules have been produced in the system, whereas on Pd 1000 HCl molecules are necessary to reach the same effect. During the poisoning by thiophene (*13*) in the same temperature range, palladium was also found to be more resistant than rhodium. A

TABLE 6

Initial Toxicity (*t*) and Relative Activity at the Steady State for Different Catalysts

Sample	Metal	Dispersion (%)	Initial toxicity, *t* (atom · $molecule^{-1}$)	Relative Activity at the steady state	HCl Pressure at the steady state (atm)
FU134	Pd	3	1×10^{-3}	0.27	5.2×10^{-3}
CGF11A	Pd	5	1.8×10^{-3}	0.16	1.7×10^{-3}
FU135	Pd	19	0.5×10^{-3}	0.38	2.4×10^{-3}
CGDA	Pd	47	0.2×10^{-3}	0.56	7×10^{-3}
CGF20A	Pd	64	0.25×10^{-3}	0.41	6.5×10^{-3}
CGF11'A	Pd	65	0.5×10^{-3}	0.44	6×10^{-3}
CGF19A	Pd	72	0.2×10^{-3}	0.25	1.6×10^{-3}
FU173	Pd	80	0.5×10^{-3}	0.60	2.9×10^{-3}
CGF16A	Rh	100	3.5×10^{-3}	0.05	3×10^{-5}
CGF3A	Rh	46	7×10^{-3}	0.09	11×10^{-5}
RAF	Rh	27	8.5×10^{-3}	0.19	43×10^{-5}
CGF15A	Rh	14	12×10^{-3}	0.12	6×10^{-5}

better resistance against chlorine is observed when the size of the metallic particles decreases. This behavior is reproduced on the two metals and will be discussed further in the light of the mechanistic considerations.

(2) A self-inhibition of the active surface by a strong but reversible interaction between HCl and the metal. This influence can be clarified by the kinetic study of the reaction.

Several mechanisms have been proposed for the reaction of dechlorination. According to Kraus and Bazant (*3*), hydrogen and chlorobenzene are adsorbed according to a Langmuir-type dissociative adsorption and the rate determining step is the reaction between adsorbed hydrogen and chlorobenzene. On metal/nylon catalysts, Dini *et al.* (*4*) concluded that the rate is controlled by the interaction between gaseous hydrogen and adsorbed chlorobenzene; in that case, the C—Cl bond could be weakened by the electron withdrawing effect of the metal. LaPierre *et al.* (*5*) propose that dechlorination proceeds by dissociative adsorption of the chloro-organic compound and hydrogen, followed by a rapid recombination between the phenyl radical and a proton.

In order to make precise the kinetic influence of the reactants and HCl, we have plotted in Figs. 3, 4, and 5 the rate of conversion of chlorobenzene over Pd/Al_2O_3 (sample FU134) as a function of the pressure of chlorobenzene, HCl, and H_2, respectively.

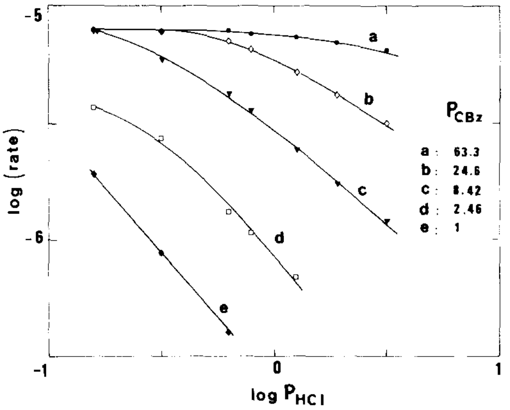


FIG. 4. Dependence of chlorobenzene conversion rate as a function of HCl pressure at different CBz pressures. T = 353 K; sample Pd/Al_2O_3 CGF11A. Pressures in Torr.

At low partial pressure of HCl, the reaction order relative to chlorobenzene varies from 1 at low pressure, to zero at high pressure of the chloro-organic compound, but no inhibition by this compound is noticed at the higher pressure. At the higher pressures of HCl, the order with respect to chlorobenzene increases to one.

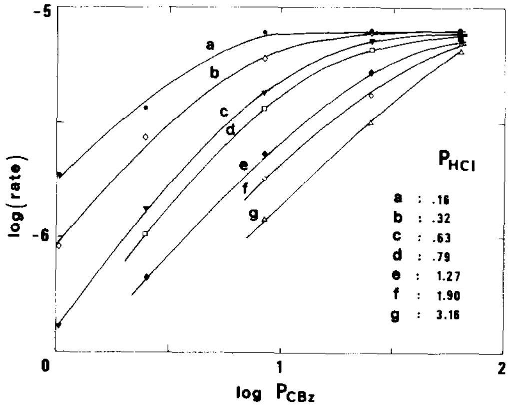


FIG. 3. Dependence of chlorobenzene conversion rate as a function of CBz pressure at different HCl pressures. T = 353 K; sample Pd/Al_2O_3 CGF11A. Pressures in Torr.

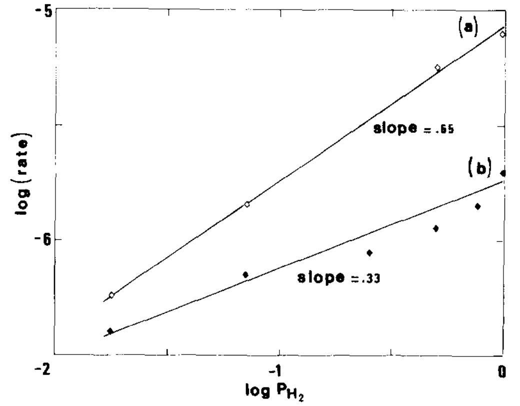


FIG. 5. Dependence of chlorobenzene conversion rate as a function of hydrogen pressure. CBz pressure: (a) 63.3 Torr, (b) 0.5 Torr; T = 353 K; sample Pd/Al_2O_3 CGF11A. H_2 pressure in atm.

The order relative to hydrogen depends on the partial pressure of chlorobenzene and decreases when the partial pressure of chlorobenzene decreases. At the higher pressure of chlorobenzene, a reaction order close to 0.5 is observed for hydrogen, which suggests dissociation.

The inhibiting effect of HCl depends on the partial pressure of chlorobenzene; at low pressure of CBz the reaction order is −1 for HCl, but reaches zero at the higher pressure of CBz.

From these observations we can draw the following conclusions:

(1) in the rate determining step hydrogen reacts in a dissociated form, which rules out the mechanism proposed by Dini *et al.* (*4*);

(2) chlorobenzene and HCl compete for adsorption and both species are strongly adsorbed.

These kinetic data are consistent with a rate determining step involving the reaction of adsorbed species. However, no inhibition by chlorobenzene could be observed at the higher partial pressures, and the observation that the reaction order relative to hydrogen varies with the partial pressure of chlorobenzene suggests a different mechanism.

Studying the conversion of fluorobenzene on tungsten films, Harper and Kemball (*2*) showed that the Arrhenius parameters corresponded to the fluorination of the metallic surface. A reaction scheme involving a chlorination/dechlorination process could also well explain the present results.

This reaction scheme is formally identical to the mechanism proposed by Mars and van Krevelen (*15*) for the selective oxidation of hydrocarbons and can be written as

$$\mathrm{Pd{-}H} + \mathrm{C_6H_5Cl_{(g)}} \xrightarrow{k_1} \mathrm{Pd{-}Cl} + \mathrm{C_6H_{6(g)}} \quad (1)$$

$$\mathrm{Pd{-}H} + \mathrm{HCl} \xrightarrow{k_2} \mathrm{Pd{-}Cl} + \mathrm{H_2} \quad (2)$$

$$\mathrm{Pd{-}Cl} + \mathrm{H_2} \xrightarrow{k_H} \mathrm{Pd{-}H} + \mathrm{HCl} \quad (3)$$

Reaction (1) probably implies the oxidative addition of chlorobenzene on the palladium atom, followed by the elimination of benzene. The surface is reduced by hydrogen in step 3, and the competition between HCl and chlorobenzene is readily explained.

At the steady state, the rates of reduction and chlorination of the surface must be equal, thus:

$$k_1\theta_H P^{\alpha}_{CBz} + k_2\theta_H P^{\beta}_{HCl} = k_H\theta_{Cl} P^{\gamma}_{H_2} \quad (4)$$

where θ_H and θ_{Cl} represent the fractional coverage of hydrogen and chlorine.

Let us assume that $\theta_H + \theta_{Cl} = 1$, since both reactants are strongly adsorbed. The rate of the reaction is then given by

$$r = \frac{k_1 k_H P^{\alpha}_{CBz} P^{\gamma}_{H_2}}{k_1 P^{\alpha}_{CBz} + k_2 P^{\beta}_{HCl} + k_H P^{\gamma}_{H_2}}. \quad (5)$$

Taking into account the experimental determinations of reaction orders, the rate law becomes

$$r = \frac{k_1 k_H P_{CBz} P^{0,5}_{H_2}}{k_1 P_{CBz} + k_2 P_{HCl} + k_H P^{0,5}_{H_2}}. \quad (6)$$

The fractional coverage by hydrogen is given by

$$\theta_H = \frac{k_H P^{0,5}_{H_2}}{k_H P^{0,5}_{H_2} + k_1 P_{CBz} + k_2 P_{HCl}}. \quad (7)$$

Under the usual conditions of working, θ_H is much lower than 1 and the major part of the surface is covered by chlorine.

The rate constants k_1, k_2, and k_H can be obtained by fitting Eq. (6) to the kinetic data, using a least squares method. This was done for several catalysts using an approach by trial and error. Figures 6 and 7 show the quality of the fit between the rates calculated from Eq. (6) and the experimental results. The correlation is generally good and sometimes excellent; in the case of rhodium a lower quality is observed, which may be accounted for by a lower activity and hence a lower precision of the determinations of the rate in that case.

In order to compare the specific activities per surface metal atom, the rate constants

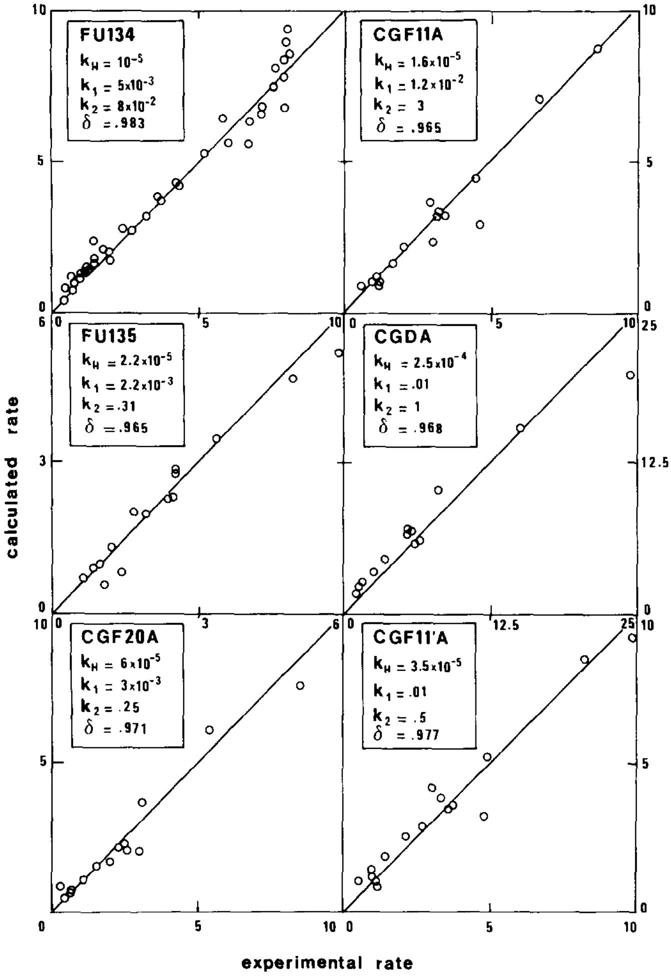


FIG. 6. Comparison of calculated and experimental rates for different catalysts; δ represents the correlation coefficient. The rates are mulitplied by 10^6.

expressed in moles · s^{-1} · g^{-1} were converted to turnover frequencies, i.e., molecules per unit time per surface metal atom. These constants, written k'_1, k'_2, and k'_H, are reported in Table 7.

The reactivity order Pd > Rh agrees with the previous report of Harper and Kemball (2) on the reaction of halobenzenes with hydrogen on Pt, Pd, Ni, and W films. These authors concluded that the metals which are the best catalysts for hydrogenating aromatic rings are also those on which less C–halogen bond rupture occurs at the temperature investigated.

HCl produced in the reaction could also interact with the support and therefore modify indirectly the properties of the metal particles. Nevertheless samples of similar dispersion, CGF19A and FU173, prepared using the chloride or a chlorine-free precursor behave similarly. It seems likely that the chlorine fixed on the support has no great influence on the catalytic properties of Pd particles in the present case.

An interesting point which appears in Table 7 is that the values of the rate constants k'_1, k'_2, and k'_H depend on the dispersion of the metal. Both reduction and chlorination rates of the surface decrease when the dispersion of the metallic phase increases.

At first sight, this behavior is surprising since reduction and chlorination have for-

TABLE 7

Specific Rate Constants (Turnover Frequencies) for the Chlorination and the Regeneration of the Metallic Particles of Different Catalysts

Sample	Metal	Dispersion (%)	Rate constants (s^{-1})		
			k'_H	k'_1	k'_2
FU134	Pd	3	3.6	1470	2.9×10^4
CGF11A	Pd	5	4.2	3180	7.9×10^4
FU175	Pd	19	1	100	1.4×10^4
CGDA	Pd	47	1.4	220	1.1×10^4
CGF20A	Pd	64	1.9	300	1.2×10^4
CGF11'A	Pd	65	1	290	1.5×10^4
CGF19A	Pd	72	0.34	34	425
FU173	Pd	80	0.17	42	850
CGF16A	Rh	100	0.5×10^{-3}	165	6700
CGF3A	Rh	45	2×10^{-3}	180	4500
RAF	Rh	27	4.1×10^{-3}	600	9000
CGF15A	Rh	14	5×10^{-3}	1500	10^5

mally an opposite character; a different evolution of these two reactions was therefore expected. However, several reports from the literature support this experimental evidence. Oxygen removal from Rh/Al_2O_3 occurs at a lower rate on small particles (*16*), and bulk Rh, Ru, or Ir chlorides are easily reduced compared with supported chlorides on alumina (*17*). Both Cl and O act as electron acceptors towards metals (*18–20*). It seems then likely that Pd and Rh covered with O or Cl present a similar behavior, and the decrease of k'_H with particle size (Table 7) can be easily understood.

However, small metallic particles are often described as electron deficient species, less reactive towards electrophilic adsorbates like Cl, O, or S (*13, 21–23*), but presenting an enhanced reactivity towards nucleophilic compounds (*24–26*). Thus it is not surprising that the chlorination rate of the metal particles decreases when the dispersion increases.

The relative behaviors of Rh/Al_2O_3 and Pd/Al_2O_3 are also consistent with their respective properties: the higher value of k'_H for Pd appears quite normal since PdO/Al_2O_3 can be reduced at a much lower temperature than Rh_2O_3/Al_2O_3 (*13*). It is also well known that rhodium is much more readily oxidized than palladium, which has a higher ionization potential. The ratios k'_1/

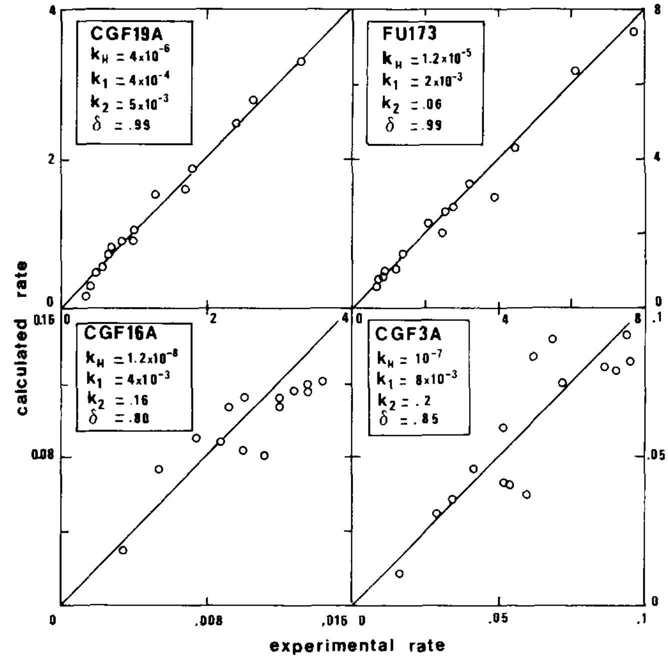
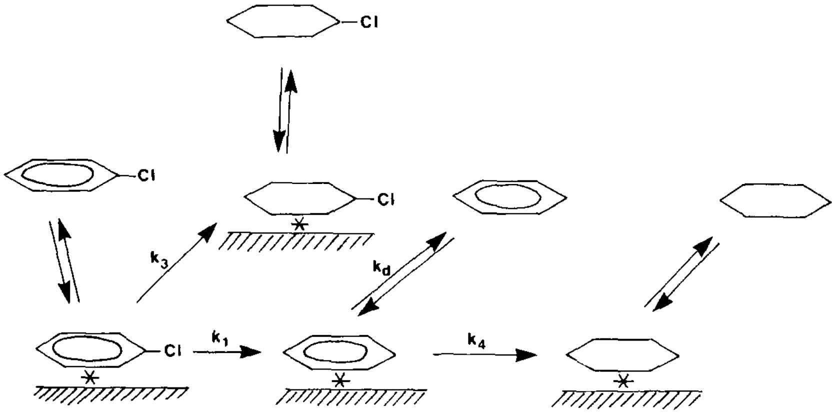


FIG. 7. Comparison of calculated and experimental rates for different catalyst; δ represents the correlation coefficient. The rates are multiplied by 10^6.

k'_H and k'_2/k'_H were therefore expected to be larger for rhodium than palladium.

According to the formal mechanism hydrogenation of the aromatic ring can occur by the parallel conversion of CBz to CCH or the consecutive conversion of Bz to CH. On Pd the former reaction is negligible and the latter rather significant; the reverse is true on Rh. The conversion of CBz may be formally described by the "rake scheme" applied by Germain to the oxidation of hydrocarbons (27):



In this scheme the selectivity to chlorocyclohexane depends on the rates k_3/k_1 and the rate of formation of benzene on the probability q of desorption of benzene, $q = k_d/(k_d + k_4)$ where k_d is the rate constant for the desorption of benzene. Therefore the rates of formation of cyclohexane and chlorocyclohexane do not follow necessarily the same trend.

On Rh the CCH yield decreases when the hydrogen coverage θ_H becomes lower (Fig. 8). At a constant θ_H value the selectivity Bz/CCH also depends on the Rh dispersion (Table 8).

The large differences observed between rhodium and palladium can be ascribed to changes in the electronic parameters governing the selectivity but the influence of both particle size and θ_H on Rh catalysts may be rationalized using another hypothesis. A 100-fold decrease of the k_3/k_1 ratio corresponds to a very small change of the chlorine coverage from 0.9900 to 0.9999. It seems little convincing that so small a modification of surface coverage by chlorine so largely influences the electronic properties of the particles. By contrast, if we assume that the yield of chlorocyclohexane depends on the hydrogen coverage, we can understand that the rate of formation of CCH is multiplied by 100 when θ_H increases from 10^{-4} to 10^{-2}. Such an interpretation also explains the effect of particle size assuming that a few neighbor hydrogen atoms are required to hydrogenate chlorobenzene; in the ensemble theory of metal catalysis the probability of encountering such an

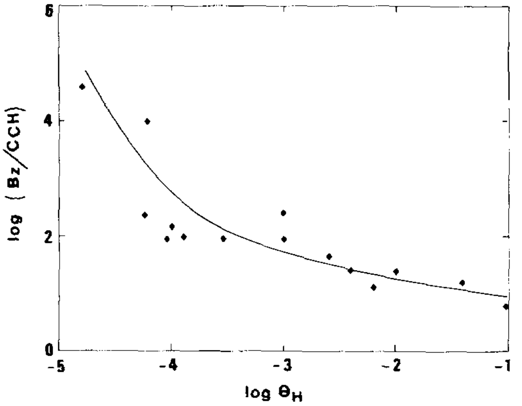


FIG. 8. Benzene/chlorocyclohexane ratio as a function of the hydrogen coverage θ_H. Sample Rh/Al_2O_3 CGF3A.

TABLE 8

Benzene/Chlorocyclohexane Ratio as a Function of the Dispersion of Rhodium Catalysts (θ_H = 10^{-3})

	Samples			
	CGF16A	CGF3A	RAF	CGF15A
Dispersion	100	45	27	14
Bz/CCH	∞	100	50	20

ensemble increases when θ_H increases at constant particle size, or when the particle size increases at constant θ_H.

Turnover frequencies (TOF) of benzene hydrogenation at 353 K have been found to be 3–7 h^{-1} for Pd/Al_2O_3 (*9, 28*) and 2000–4000 h^{-1} for Rh/Al_2O_3 (*10, 28*). In the present case the TOF of secondary reaction giving CH from Bz ranges from 100 to 150 h^{-1} for Pd/Al_2O_3 and 1 h^{-1} for Rh/Al_2O_3. The orders of reactivity are then completely reversed between Rh and Pd: palladium is promoted by chlorine whereas Rh is severely inhibited. This points out the importance of electronic interactions in these reactions of halohydrocarbons.

CONCLUSIONS

The reaction scheme of CBz conversion is formally similar to that generally assumed for the oxidation of hydrocarbons: chlorobenzene and HCl interact with the surface to form a surface metal chloride, and hydrogen cleans the surface. Both rates of chlorination and reduction of the metallic surface decrease when the metal particle size decreases. This behavior seems to be related with the electrodeficient character of small aggregates.

Chlorine removal from CBz is a highly selective process, since hydrogenation of the aromatic ring to CCH represents less than 0.1% on Pd/Al_2O_3 and 5% on Rh/Al_2O_3. On this latter metal the selectivity ratio Bz/CCH depends on the size of the metallic particles of the catalyst. It has been observed that the formation of CCH increases with the hydrogen coverage.

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