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Hydrodechlorination of 1,1-Bis(*p*-chlorophenyl)-2,2-dichloroethylene (*p,p′*-DDE) in the Vapor Phase

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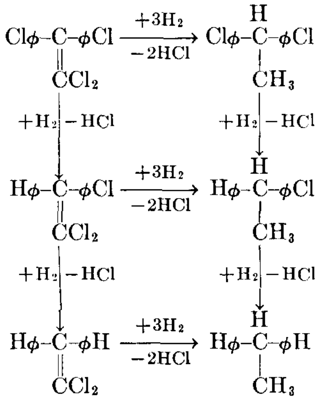
The catalytic hydrodechlorination of 1% solutions in xylene of 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethylene (*p,p′*-DDE) and the corresponding ethane (*p,p′*-DDD) were studied in a continuous gas-phase reactor over a prereduced 0.35-wt% Pd on α-Al_2O_3 catalyst at 170–230°C, 40–670 Torr of H_2. Reaction stoichiometry for DDE was a network characterized either by the addition of one H_2 to remove one aromatic chlorine at a time or by addition of $3H_2$, resulting in removal of two olefinic chlorines and olefin saturation. This latter process proceeds without measurable desorption of intermediates such as substituted ethylidene dichlorides, vinylchlorides, ethylchlorides, or ethylenes.



Olefinic hydrocechlorination is a precursor to hydrogenation of the dechlorinated olefin. Selectivity analyses by reaction path methods established relative reaction rates for each step. The reactions were first order in hydrogen for aromatic hydrodechlorination. Rate data were fitted by Langmuir–Hinshelwood kinetics, in which xylene inhibits the surface reaction.

INTRODUCTION

There have been studies on the catalytic hydrodechlorination of chlorinated organics by the general reaction

$$R\text{-}Cl + H_2 \xrightarrow{\text{catalyst}} R\text{-}H + HCl$$

in both gas and liquid phases. The most commonly used catalysts are supported group VIII metals. Weiss and Krieger (*1*) studied the gas-phase hydrodechlorination of *cis*- and *trans*-dichloroethylenes and vinyl chloride over a Pt on η-Al_2O_3 catalyst. Kammerer *et al.* (*2*) and Horner *et al.* (*3*) studied the hydrogenolysis in liquid phase

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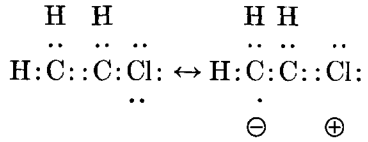
of aromatic and aliphatic halogens, respectively, in the presence of Raney nickel and alkali. These studies established that primary and secondary monochloroalkanes were essentially nonreactive, vicinal saturated dichloro compounds reacted slowly, and compounds with chlorine adjacent to a double or triple bond reacted readily. Kraus and Bazant (*4*) studied the hydrodechlorination of a series of substituted chlorobenzenes both over Pd on carbon catalyst in the vapor phase and by using sodium aluminum hydride in the liquid phase. They correlated rate data using the Hammett equation.

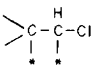
It is found in hydrodechlorination that aromatic and olefinic chlorines are highly reactive and that aliphatic chlorine is essentially nonreactive. Such observations are the opposite of the usual rules in organic chemistry, where aliphatic chlorides are found to be highly reactive and olefinic and aromatic chlorides are relatively unreactive.

Coulson (*5*) suggested that olefinic and aromatic carbon–chlorine bonds acquire a distinct double-bond character as the chlorine atom loses Π electrons due to resonance, as illustrated in the case of vinyl chloride:

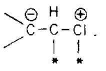


$$\mathrm{H{:}\overset{\textstyle H}{\overset{..}{C}}{::}\overset{\textstyle H}{\overset{..}{C}}{:}\underset{..}{\overset{..}{Cl}}{:}} \leftrightarrow \mathrm{H{:}\overset{\textstyle H}{\overset{..}{C}}{:}\underset{\ominus}{\underset{\cdot}{\overset{\textstyle H}{\overset{..}{C}}}}{::}\underset{\oplus}{\overset{..}{Cl}}{:}}$$

To explain hydrodechlorination reactions, a mechanism was proposed by Weiss and Krieger in which it was assumed that olefinic chlorides are adsorbed on the catalyst as stabilized resonance forms, best represented as structures containing either

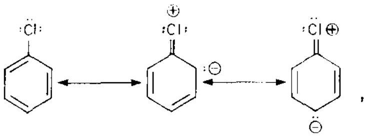


or

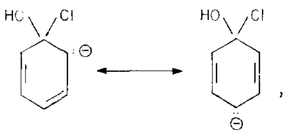


Hydrogenation was postulated to proceed by molecular hydrogen addition to the carbon–carbon bond of one form, and hydrodechlorination by proton addition to the carbon–chlorine bond of the other form. The catalyst was regarded as a device to stabilize the charge distribution of the resonating molecule. The double-bond character of the carbon–chlorine bond is manifested by C–Cl shortening in olefinic and aromatic chlorides. The double-bond character of olefinic chlorides and dichlorides was calculated by Pauling (*6*) to be 18%, based on the olefinic chloride C–Cl bond length of 1.69 Å. This is compared to a 1.76-Å C–Cl bond length in aliphatic chlorides. Both Morrison and Boyd (*7*) and Gould (*8*) discuss in their texts the justification for and the nature of the carbon–chlorine bond double-bond concept.

The carbon–chlorine double bond explains the *non*reactivity of aryl and vinyl halides in nucleophilic substitution. The resonance structures for chlorobenzene involve



a Π electron system having seven atoms. Nucleophilic attack (e.g., OH⁻) gives



and the Π electron system involves only five atoms. Therefore this process is unfavorable. Note again that these results are reversed for catalytic hydrodechlorination.

In this work the hydrodechlorination of DDE and DDD was studied as part of an Environmental Protection Agency-sponsored program on the "Catalytic Conversion of Hazardous and Toxic Chemicals" (EPA Contract R 802-857-01) (*9*). The system studied simulated the gas-phase,

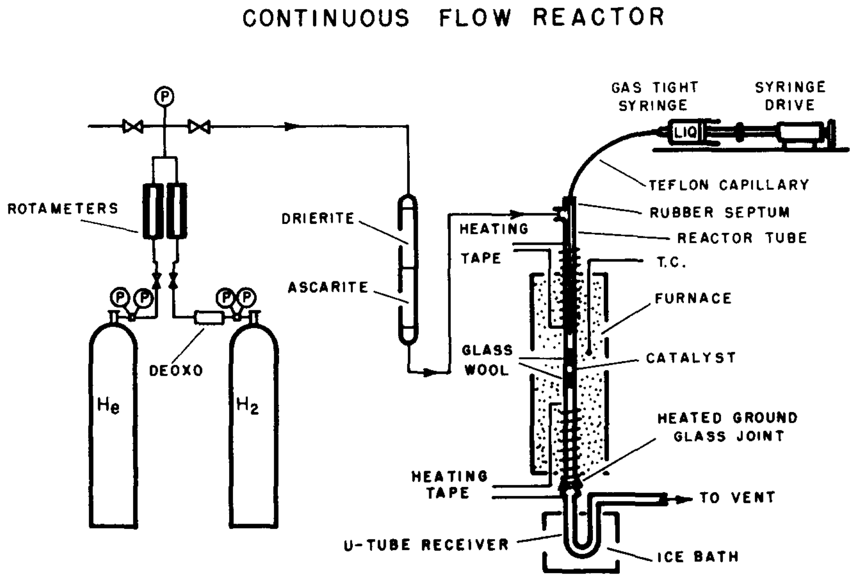


FIG. 1. Continuous flow back-mixed reaction system. Note that joint between reactor and product receiver was heated to prevent product condensation before the receiver.

low-pressure, continuous-flow detoxification reaction of DDT solution in xylene that would be obtained by solvent extraction from formulated insecticides.

Pd was chosen as the active component since it is known (*10*) that Pd is the most active hydrodechlorination catalyst, while being relatively inactive for aromatic hydrogenation(*11*) and hydrogenolysis (*12*). α-Al_2O_3 was chosen as the support to minimize pore diffusion effects. The average pore diameter for this support is reported (*13*) to be in the range of 2.0 to 0.5 μm.

MATERIALS AND METHODS

Hydrogen and helium (both >99.9%) used for this work were obtained from Airco and American Industrial & Medical Products, Inc., respectively. Hydrogen was passed over Pd Deoxo catalyst to remove traces of oxygen. Water and CO_2 present in the gas streams were removed by a Drierite/Ascarite bed. *p*-Xylene (Aldrich Spectro Grade) was used as a solvent for the reactants. DDD (Chem Service CP Grade) and DDE prepared by dehydrochorination by NaOH reaction with DDT (Montrose Technical Grade) were used as reactants. Both reactants had a chromatographic purity of >99%. The catalyst used was Girdler 7573-S 0.35-wt% Pd on α-Al_2O_3 with a nitrogen BET surface area of 9.6 m^2/g.

Figure 1 is a diagram of the continuous reaction system used for this study. Sets of experiments were performed where (i) hydrogen partial pressures were adjusted by varying the hydrogen to helium ratio at constant total gas and liquid flow rate, (ii) DDE partial pressures were adjusted by varying the liquid feed rate from 0.02 to 0.11 ml/min at a fixed gas flow rate, and (iii) space time[2] was adjusted by varying total gas flow rate from 30 to 60 standard cc/min. The reactant solutions were pumped by a Harvard Apparatus compact infusion pump equipped with a 50-ml Hamilton gas-tight syringe. The reactor was fabricated from 6-mm-i.d. Pyrex tubing mounted vertically in an electric furnace. Heating tape was wrapped on each end of the reactor to give individual control of the

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[2] Space times were calculated assuming ideal gas behavior at 0°C and 1 atm of total pressure.

feed vaporization and product collection temperatures. The $\frac{1}{16}$-in.-diameter Teflon feed line from the syringe extended into the reactor to a point where it was isothermal with the catalyst to avoid DDE deposition on the reactor walls. Catalyst beds, typically 1 to 3 mm long containing 20–30 mg of 60- to 80-mesh catalyst, were positioned in the isothermal zone of the furnace and retained by plugs of Pyrex wool. The product stream was collected in a 0°C cold trap connected to the outlet of the reactor by a heated ground-glass joint. This arrangement was needed to remove the total product solution without loss due to crystallization before the product receiver.

Four different catalyst charges were used for the DDE experiments. Each catalyst was reduced for at least 2 hr at 200°C in flowing hydrogen. Stable activity was obtained approximately 10 hr after the liquid feed (17% DDE in *p*-xylene) was introduced. Initial selectivities were similar to those observed over the stable catalyst. Each catalyst was used for 3–4 days. Each day one process variable was investigated. The catalyst was purged with hydrogen between each day's experiment.

Aging studies showed that activity loss as measured by decrease in total chlorine conversion was <2% per day. Carbonaceous deposits on the catalyst were not observed, nor were high-boiling oligomerization products.

Analysis

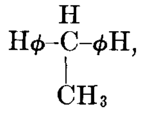
GC-MS techniques provided quantitative identification of all reactants and products. The equipment used was a Perkin–Elmer 900 dual F. I. D. gas chromatograph interfaced with a duPont 21-491 double-focusing mass spectrometer. Chromatographic separations were carried out on a 3-m × $\frac{1}{8}$-in. 3% OV-17 on 80- to 100-mesh Chromasorb W (HP) column. Helium flow rate was 30 ml/min, and the column was temperature-programmed from 152 to 250°C at 5°C/min. Data reduction was carried out on a Columbia Scientific Industries CSI-208 automatic digital integrator. Analysis of the liquid product showed that neither hydrogenation, dealkylation, nor cracking of the solvent, *p*-xylene, occurred and that recovery of 1,1-diphenylethane/ethylene nuclei was quantitative. Within the limit of experimental error, the volume of reactant solution delivered equaled that of the product solution received. Details of the analysis are included in the final report for this project, submitted to the Environmental Agency (*9*).

Mass Transfer Characteristics

Based on correlations by Wilke and Lee (*14*, *15*) and using the calculation procedure of Satterfield (*16*) both the bulk and effective pore diffusivities of DDE were calculated. Using the criterion of Weisz and Prater (*17*), it was determined that DDE reaction rates were two orders of magnitude lower than those required for the onset of pore diffusion limitations (mainly as a consequence of the low-surface-area catalyst used). Calculation of the degree of dispersion (*18*) in the reactor showed the reactor to be essentially back-mixed by diffusion. Selectivity analyses using both back-mixed and plug flow models were tested, and selectivity data from low to high conversion could only be fitted with the back-mixed model.

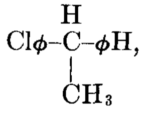
RESULTS

Five major DDE hydrodechlorination products were observed, i.e., 1,1-diphenylethane,



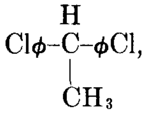
$$\mathrm{H}\phi\text{–}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}\text{–}\phi\mathrm{H}, \qquad \text{(I)}$$

1-*p*-chlorophenyl-1-phenylethane,



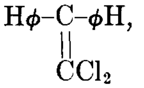
$$\mathrm{Cl}\phi\text{–}\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}\text{–}\phi\mathrm{H}, \qquad \text{(II)}$$

1,1-bis(*p*-chlorophenyl)-ethane,



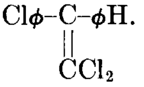
$$\mathrm{Cl}\phi\text{–}\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{–}\phi\mathrm{Cl}, \qquad \mathrm{(III)}$$

1,1-diphenyl-2,2-dichloroethylene,



$$\mathrm{H}\phi\text{–}\underset{\overset{\|}{\mathrm{CCl_2}}}{\mathrm{C}}\text{–}\phi\mathrm{H}, \qquad \mathrm{(IV)}$$

and 1-*p*-chlorophenyl-1-phenyl-2,2-dichloroethylene,

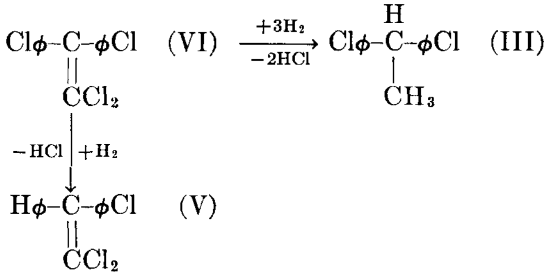


$$\mathrm{Cl}\phi\text{–}\underset{\overset{\|}{\mathrm{CCl_2}}}{\mathrm{C}}\text{–}\phi\mathrm{H}. \qquad \mathrm{(V)}$$

Only minor amounts of diphenylethylenes containing 0, 1, and 2 aromatic chlorines were observed at low conversions. 2-Chloro-1,1-diphenylethylenes–ethanes were not observed.

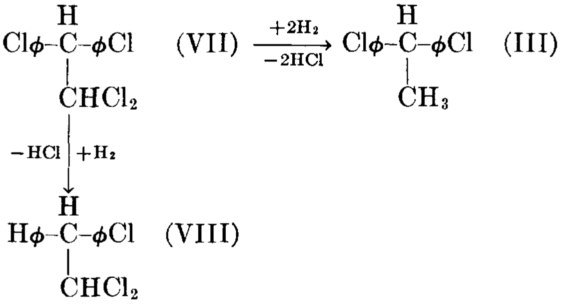
Chlorine conversion was used as an extent of reaction parameter and is defined as $(4 - \phi)/4$, where $\phi = \sum_{h=0}^{4} h(\mathrm{Cl}_h)$, 4 = initial number of chlorine atoms per molecule of reactant, h = number of chlorine atoms per molecule of product and unconverted reactant, and Cl_h = relative mole fraction of compounds with h chlorine atoms per molecule. Figures 2 and 3 are typical selectivity plots (product distribution vs chlorine conversion) for DDE and DDD hydrodechlorination, respectively. These results were obtained at 200°C, $P_{\mathrm{H_2}}$ of 580 ± 90 Torr and from 0.0244 to 0.0609 sec. Plots of selectivity data obtained at other experimental conditions showed similar behavior and correlation to calculated reaction paths (as discussed later).

Compounds V and III are both initial DDE reaction products, i.e.:



$$\begin{tikzcd} \mathrm{Cl}\phi\text{–}\underset{\overset{\|}{\mathrm{CCl_2}}}{\mathrm{C}}\text{–}\phi\mathrm{Cl}\ \mathrm{(VI)} \arrow[r, "+3\mathrm{H_2}", "-2\mathrm{HCl}"'] \arrow[d, "-\mathrm{HCl}"', "+\mathrm{H_2}"] & \mathrm{Cl}\phi\text{–}\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{–}\phi\mathrm{Cl}\ \mathrm{(III)} \\ \mathrm{H}\phi\text{–}\underset{\overset{\|}{\mathrm{CCl_2}}}{\mathrm{C}}\text{–}\phi\mathrm{Cl}\ \mathrm{(V)} & \end{tikzcd} \qquad (1)$$

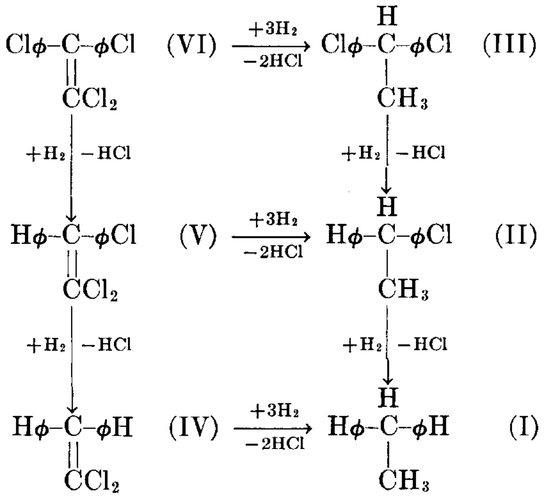
Similar behavior is observed with DDD, i.e.;



$$\begin{tikzcd} \mathrm{Cl}\phi\text{–}\overset{\mathrm{H}}{\underset{\mathrm{CHCl_2}}{\mathrm{C}}}\text{–}\phi\mathrm{Cl}\ \mathrm{(VII)} \arrow[r, "+2\mathrm{H_2}", "-2\mathrm{HCl}"'] \arrow[d, "-\mathrm{HCl}"', "+\mathrm{H_2}"] & \mathrm{Cl}\phi\text{–}\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{–}\phi\mathrm{Cl}\ \mathrm{(III)} \\ \mathrm{H}\phi\text{–}\overset{\mathrm{H}}{\underset{\mathrm{CHCl_2}}{\mathrm{C}}}\text{–}\phi\mathrm{Cl}\ \mathrm{(VIII)} & \end{tikzcd} \qquad (2)$$

In both cases aromatic hydrodechlorination proceeds in parallel with removal of the two olefinic/aliphatic chlorines. Simultaneous removal of both aromatic chlorines or aromatic and olefinic/aliphatic chlorine was not observed under these conditions. Oligomerization and ring saturation side reactions were not observed in products. Hydrogenation of DDE to DDD was not observed, which indicates that olefinic hydrodechlorination is a precursor to hydrogenation of the dechlorinated olefin.

Based on the observed stepwise removal of aromatic chlorine and the parallel removal of olefinic chlorine the following network described the stoichiometry for DDE hydrodechlorination:



$$\begin{tikzcd}
Cl\phi\text{-}\overset{}{\underset{\underset{CCl_2}{\|}}{C}}\text{-}\phi Cl\ (VI) \arrow[r, "+3H_2"', "-2HCl"] \arrow[d, "+H_2"', "-HCl"] & Cl\phi\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\phi Cl\ (III) \arrow[d, "+H_2"', "-HCl"] \\
H\phi\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\phi Cl\ (V) \arrow[r, "+3H_2"', "-2HCl"] \arrow[d, "+H_2"', "-HCl"] & H\phi\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\phi Cl\ (II) \arrow[d, "+H_2"', "-HCl"] \\
H\phi\text{-}\underset{\underset{CCl_2}{\|}}{C}\text{-}\phi H\ (IV) \arrow[r, "+3H_2"', "-2HCl"] & H\phi\text{-}\overset{H}{\underset{\underset{CH_3}{|}}{C}}\text{-}\phi H\ (I)
\end{tikzcd} \quad (3)$$

In the absence of adsorption–desorption and pore diffusion disguises discussed by Wei (*19*), the catalytic selectivities observed in a coupled reaction system can usually be described by a system of relative first-order equations. A detailed discussion has been presented by Beranek (*20*). However, it may be necessary to describe the absolute rate of reaction of any one species by a functionality that is quite different. This type of behavior is the consequence of the system's obeying Langmuir-type rate expressions consisting of first-order functionality in the numerator and a surface term in the denominator, which is common to each rate expression.

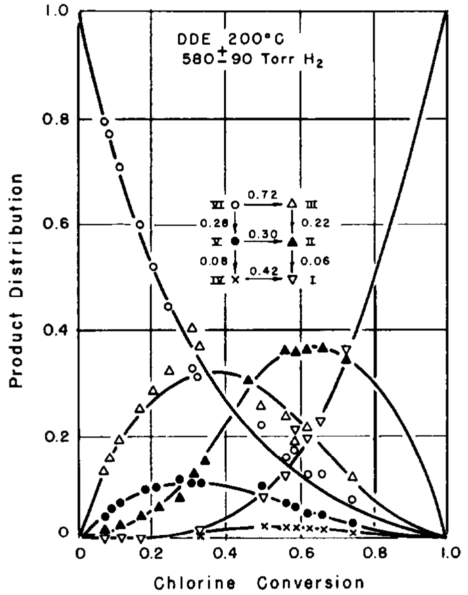


FIG. 2. DDE hydrodechlorination selectivity at 200°C and 580 ± 90 Torr. Lines were calculated based on the relative rate constants indicated on the reaction network.

In these studies the rate of each unidirectional hydrodechlorination step i → j is of the form

$$r_{ij} = \frac{k_{ij}K_iP_iP_{H_2}^{n \text{ or } m}}{(1 + \Sigma K_iP_i)^b}, \tag{4}$$

where k_{ij} = intrinsic rate constant to react from species i to species j, K_i = adsorption equilibrium constant for species i in the system (including nonreactants), n or m = order in H_2 for aromatic and olefinic chlorine removal, respectively, b = an exponent, and P_i = gas phase partial pressure of species i. All experiments reported here were conducted at constant pressure and in a large excess of hydrogen so that the $P_{H_2}^{n \text{ or } m}$ terms were effectively constant. Therefore each group $k_{ij}K_iP_{H_2}^{n \text{ or } m}$ may be lumped into a first-order pseudohomogeneous rate constant k'_{ij}. Since the surface is identical for all species, the surface terms $(1 + \sum K_iP_i)^b$ will cancel when rates are divided and relative rate constants for a selectivity network are calculated.

The reaction network for DDE,

$$\begin{tikzcd}
(\mathrm{VI}) \arrow[r, "k'_{63}"] \arrow[d, "k'_{65}"] & (\mathrm{III}) \arrow[d, "k'_{32}"] \\
(\mathrm{V}) \arrow[r, "k'_{52}"] \arrow[d, "k'_{54}"] & (\mathrm{II}) , \arrow[d, "k'_{21}"] \\
(\mathrm{IV}) \arrow[r, "k'_{41}"] & (\mathrm{I})
\end{tikzcd} \tag{5}$$

is then described by the following set of relative rate expressions (Eqs. 6–10), where r^*_i in this back-mixed system is the measured rate of production of species i (r_i) divided by the measured rate of conversion of species VI, DDE ($-r_{VI}$). For clarity, Roman numerals are used for production rates and partial pressures of species, and arabic numerals for constants for reaction from species i to j.

$$r^*_V = \frac{r_V}{-r_{VI}} = \frac{k'_{65}P_{VI} - (k'_{54} + k'_{52})P_V}{(k'_{65} + k'_{63})P_{VI}} \tag{6}$$

$$r^*_{IV} = \frac{r_{IV}}{-r_{VI}} = \frac{k'_{54}P_V - k'_{41}P_{IV}}{(k'_{65} + k'_{63})P_{VI}} \tag{7}$$

$$r^*_{III} = \frac{r_{III}}{-r_{VI}} = \frac{k'_{63}P_{VI} - k'_{32}P_{III}}{(k'_{65} + k'_{63})P_{VI}} \tag{8}$$

$$r^*_{II} = \frac{r_{II}}{-r_{VI}} = \frac{k'_{32}P_{III} + k'_{52}P_V - k'_{21}P_{II}}{(k'_{65} + k'_{63})P_{VI}} \tag{9}$$

$$r^*_I = \frac{r_I}{-r_{VI}} = \frac{k'_{21}P_{II} + k'_{41}P_{IV}}{(k'_{65} + k'_{63})P_{VI}}. \tag{10}$$

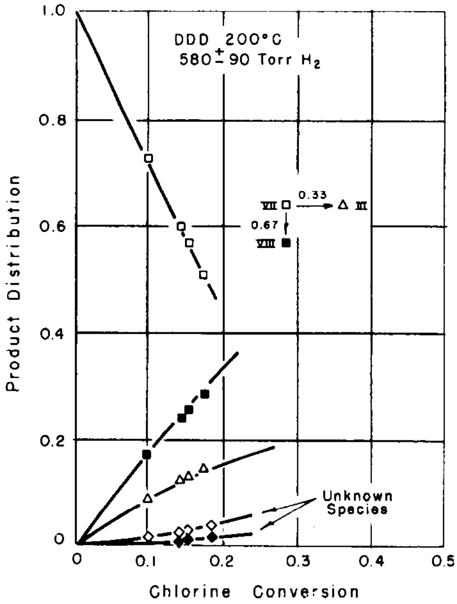


FIG. 3. DDD hydrodechlorination reaction selectivity at 200°C and 580 ± 90 Torr. Relative rate constants were calculated based on the slopes of the lines drawn.

In order to establish the relative rate constants, the normalization is made that $(k'_{65} + k'_{63}) = 1$. Defining relative partial pressure p^*_i as P_i/P_{VI}, Eqs. 6 to 10 are linearized. Relative rates can be plotted vs appropriate relative concentrations. Empirically fitted slopes and intercepts established the relative rate constants, which are the pseudohomogeneous rate constants $k'_{ij} = K_ik_{ij}P_{H_2}^{n \text{ or } m}$ where n and m are the orders in hydrogen for aromatic and olefinic chlorine removal, respectively. This is done in Fig. 4.

Since the amounts of species IV were so small, the values of k'_{41} and of the ratio k'_{52}/k'_{54} were estimated by empirically fitting the observed selectivity data for DDE in Fig. 2.

These relative rate constant values were then used to calculate the selectivity curves drawn in Fig. 2. Adjustments of the order of ±0.02 to values determined from Fig. 4 were required to obtain the excellent fit of the experimental data seen in Fig. 2. The values of the constants were determined in

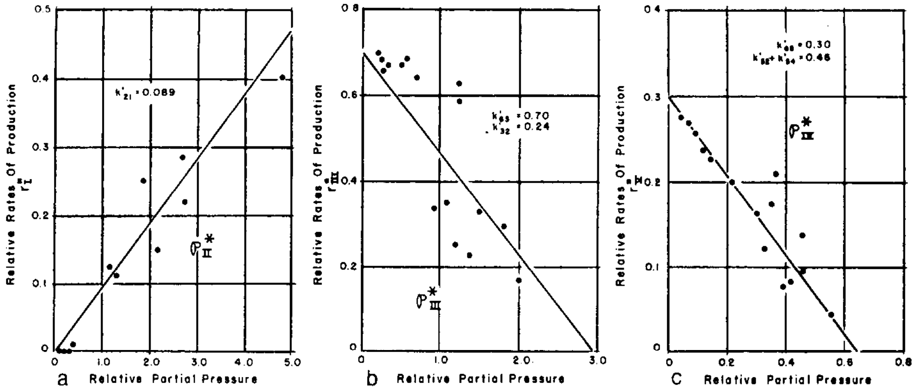


FIG. 4. Measured relative rates of production of the indicated species plotted against relative partial pressures provide the basis for estimating DDE relative rate constants.

this way for several different experimental conditions and are listed in Table 1.

The data in Table 1 show that the relative rate of olefinic to aromatic hydrodechlorination, k'_{63}/k'_{65}, is relatively insensitive to temperature over the range 170 to 230°C at 580 ± 90 Torr of H_2, indicating similar activation energies for both reactions. However, this ratio is a function of P_{H_2}, since the ratio k'_{63}/k'_{65} is proportional to $P_{H_2}^n/P_{H_2}^m$, where n and m are the hydrogen orders for olefinic and aromatic hydrodechlorination, respectively. The slope of a log–log plot of k'_{63}/k'_{65} vs P_{H_2} equals $(n - m)$. Figure 5 shows that $(n - m) = 0.5$, or the olefinic reaction is 0.5 order more hydrogen dependent than the aromatic reaction. Table 1 also shows that the aromatic hydrodechlorination reaction is retarded by removal of olefinic chlorine by comparing the values of k'_{65} and k'_{32}.

A number of DDE reaction rate expressions of the type

$$-r_{\mathrm{DDE}} = \frac{k_a P_{\mathrm{H_2}}^x P_{\mathrm{DDE}}^y + k_o P_{\mathrm{H_2}}^{x+0.5} P_{\mathrm{DDE}}^y}{P_{\mathrm{xylene}}^x},$$

where subscripts a and o refer to aromatic and olefinic hydrodechlorination of DDE, respectively, were evaluated; e.g., $x = 0$, 0.5; $y = 0$, 1; and $z = 0$, 1, 2. The best results were obtained with the following

TABLE 1

Pseudohomogeneous Relative Rate Constants

Temperature (°C)	200			170	230
P_{H_2} (Torr)	60 ± 20	140 ± 30	580 ± 90	580 ± 90	580 ± 90
k'_{65}	0.63	0.44	0.28	0.28	0.34
k'_{63}	0.37	0.56	0.72	0.72	0.66
k'_{54}	0.17	0.15	0.08	—[a]	0.18
k'_{52}	0.59	0.55	0.30	0.32	0.22
k'_{41}	—[a]	0.46	—[a]	—[a]	0.29
k'_{32}	0.12	0.32	0.22	0.02	0.23
k'_{21}	—[a]	0.09	0.06	—[a]	0.03

[a] Insufficient data to give accurate estimate.

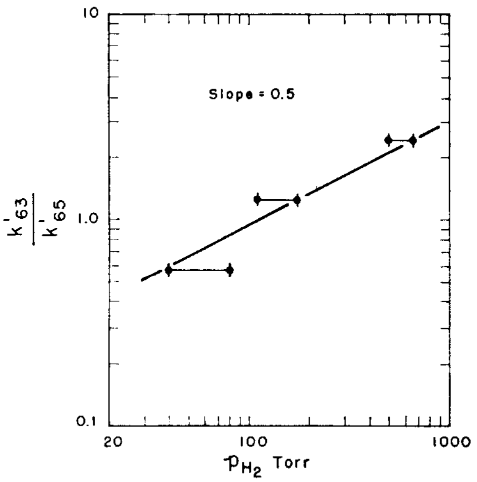


FIG. 5. Olefinic hydrodechlorination and saturation is 0.5 order more pressure dependent than aromatic hydrodechlorination at 200°C.

functionality

$$-r_{\text{DDE}} = \frac{k_a P_{\text{H}_2}^{0.5} P_{\text{DDE}} + k_0 P_{\text{H}_2} P_{\text{DDE}}}{P_{\text{xylene}}^2},$$

as shown in Fig. 6.

This behavior suggests that both the aromatic and olefinic reactions are bimolecular surface reactions, where the surface term $(1 + K_i P_i)^2$ is dominated by the $K_{\text{xylene}} P_{\text{xylene}}$ term.

It should be noted that even though the effect of the xylene solvent on absolute rate is profound, in principle it should exert no effect on relative rates and hence selectivities. This is because, as already noted, surface terms in rate expressions cancel when the equations are divided. However, this point was not experimentally tested by operating in the absence of solvent. From the selectivity analysis

$$\frac{k'_{65}}{k'_{63}} = \frac{k_{65} K_6 P_{\text{H}_2}^{0.5}}{k_{63} K_6 P_{\text{H}_2}} = \frac{0.28}{0.72}$$

at 580 Torr of H_2. Therefore, the ratio of the intrinsic rate constant may be calculated:

$$\frac{k'_{65}}{k'_{63}} = 9.4 \text{ Torr}^{0.5}$$

This value compares favorably to that obtained from the absolute rate data for the ratio of aromatic to olefinic hydrodechlorination:

$$\frac{k_a}{k_o} = \frac{0.233}{0.0221} = 10.5 \text{ Torr}^{0.5}$$

Figure 3 is a plot of the DDD selectivity data. These results were obtained at 200°C, 580 ± 90 Torr, and space times from 0.0582 to 0.0674 sec. At $P_{\text{H}_2} = 671$ Torr, $P_{\text{DDD}} = 0.295$ Torr, and $P_{\text{xylene}} = 88.3$ Torr, the DDD reaction rate was 6.73×10^{-6} mol/cm³ of catalyst min vs DDE reaction rate

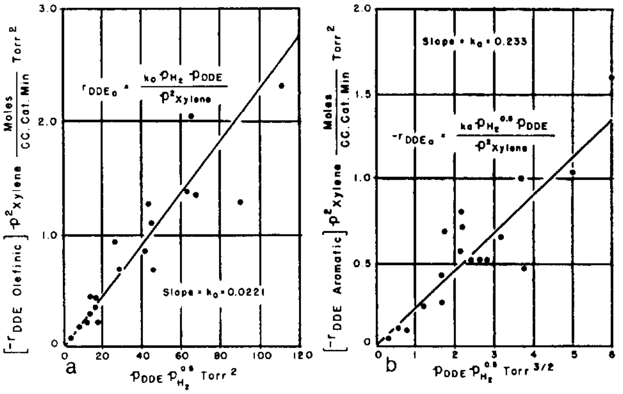
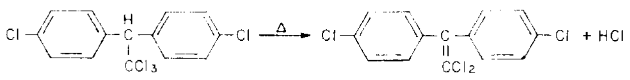


FIG. 6. Determination of the absolute kinetics for DDE hydrodechlorination at 200°C over 0.35% Pd on α-Al₂O₃.

of 16.5×10^{-6} at identical conditions. DDD is much less reactive than DDE, mainly because at these conditions the saturated aliphatic chlorines react at only half the rate that the aromatic chlorine does. That is, $k'_{73}/k'_{78} = 0.33/0.67$. The first step for DDE at these conditions is $k'_{63}/k'_{65} = 0.72/0.28$. This behavior illustrates that aliphatic chlorine reacts far slower than olefinic chlorine. As in the case of DDE, the chlorines are removed from the aromatic nuclei more slowly when there is no olefin present. The DDD results substantiate that the olefinic chlorides on DDE are removed first and then the ethylene group is saturated to ethane.

Note in Fig. 3 that there are unidentified trace species indicated, which are consecutive reaction products of species III and VIII. The pseudohomogeneous rate constant ratios were determined graphically from the data in Fig. 3.

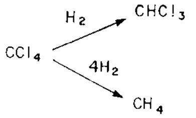
Since DDT dehydrochlorinates almost immediately to DDE, these DDE results are applicable to DDT hydrodechlorination. In pulse microreactor experiments (*9*) it was observed that thermal dehydrochlorination of DDE commenced at space times on the order of 0.01 sec at 190°C:



The DDT dehydrochlorination reaction is also catalyzed by α-Al_2O_3, so that complete conversion of DDT to DDE was obtained at a space time of 0.01 sec and 220°C in the presence of α-Al_2O_3.

DISCUSSION

In earlier work on carbon tetrachloride (*21*), it was observed that hydrodechlorination proceeded as two parallel reactions:

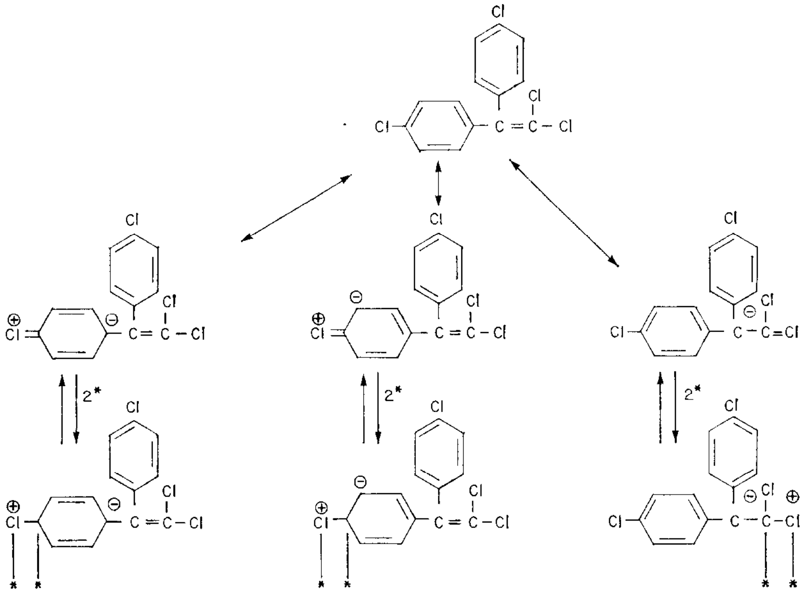


It was shown that this was not because of intermediates not desorbing. The expected intermediates $CHCl_3$, CH_2Cl_2, and CH_3Cl showed no reactivity at the same conditions. It was concluded that the addition of $4H_2$ to CCl_4 proceeded as one "concerted" set of events on the catalyst.

This type of behavior is seen in the DDE reaction network. Reaction with $3H_2$ occurs with no intermediate observed. It is clear from the low relative reactivity with DDD that —$CHCHCl_2$ is not a particularly reactive intermediate. The behavior of DDE is analogous to CCl_4, in that the "concerted" behavior again is not explained by strong adsorption of intermediates.

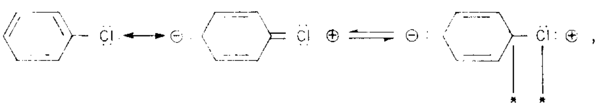
The observed products of DDE hydrodechlorination provide some insight as to the adsorbed states of DDE. In these studies, removal of aromatic and olefinic chlorine by separate routes is observed, indicating that there are two types of adsorbed states for DDE. One involves adsorption of an aromatic moiety and the other adsorption of the olefinic moiety. This behavior may also be influenced by the relatively large amount of adsorbed xylene which might not allow the whole DDE molecule to be adsorbed in a planar configuration.

The resonance forms and adsorbed configurations of DDE can be postulated by analogy with chlorobenzene and vinyl chloride:

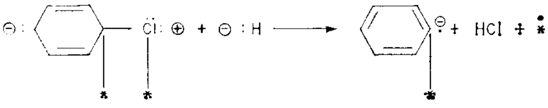


Moyes and Wells (*22*) review deuterium exchange reactions of benzene. Both dissociative and addition–abstraction mechanisms for deuterium exchange are reversible processes. Hydrodechlorination is irreversible. Since, as noted, neither chlorine exchange nor deuterium exchange on the ring occurs, exchange reaction mechanisms cannot be invoked for hydrodechlorination. Kraus and Bazant (*4*) show that the hydrodechlorination reaction of chlorobenzene is accelerated by substituents that withdraw electrons from the ring. This can be interpreted as the ability of electron withdrawing groups to stabilize the carbon–chlorine double bond. They also observed *no* disproportionation between bromobenzene and *p*-chlorotoluene at high hydrodechlorination conversion, indicating that adsorption was not dissociative. Also when *p*-chlorotoluene was reacted with D_2, only *p*-deuterotoluene was observed, suggesting interaction through the chloro substituent, not the ring.

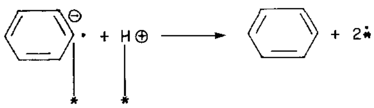
Aromatic hydrodechlorination of DDE is most likely characterized by addition of dissociated hydrogen, as suggested by the observed 0.5 order hydrogen dependence. Weiss and Krieger (*1*), as well as Kraus and Bazant (*4*), concluded that the dissociated hydrogen was in the form of protons. These latter also justified the presence of hydride ion and cite references for the existence of hydridic species on Group VIII metals. On the basis of such considerations, the mechanism for aromatic chlorine hydrodechlorination is that first a 1–2 diadsorbed species is formed,



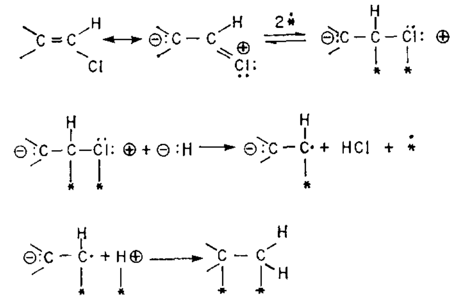
which is attached by a hydride ion,



giving rise to an adsorbed phenyl radical which combines rapidly with a proton:

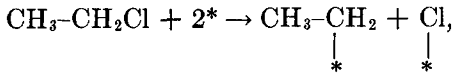


Kraus and Bazant show that aromatic exchange with deuterium does not occur, indicating little interaction between the ring and the surface.



The adsorbed ethylene radical readily reacts, and since it is already adsorbed and is itself an adsorbed olefin, it readily hydrogenates to ethane. Hence no ethylene is observed in the bulk phase.

By comparison, relatively unreacting aliphatic chlorides must undergo dissociative adsorption, and a radical type mechanism, e.g.,

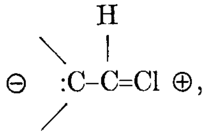


$$CH_3\text{-}CH_2Cl + 2^* \rightarrow \underset{*}{\underset{|}{CH_3\text{-}CH_2}} + \underset{*}{\underset{|}{Cl}},$$

must be the rate-controlling step.

CONCLUSIONS

The results of the DDE reaction study clearly show that the same reactivity behavior for hydrodechlorination exists on one polychlorinated molecule with different types of chlorine bonding as on separate different molecules with these same types. Olefinic and aromatic chlorines are hydrodechlorinated readily, aliphatic chlorines only with difficulty. The relative rate of olefinic to aromatic chlorine removal from DDE increases with hydrogen partial pressure from 0.37/0.28 at 60 Torr to 0.72/0.28 at 580 Torr.

Because of charge delocalization to form a carbon–chlorine double bond  $\ominus\ :\overset{\overset{H}{|}}{C\text{-}C}{=}Cl\ \oplus$, both chlorine atoms of DDE adsorbed at the olefin group are reacted away, and only then is the adsorbed olefin rapidly hydrogenated. Thus, "concerted" behavior, in which three hydrogen molecules react with DDE in one step, is observed. This is identical to concerted behavior reported for CCl_4, which reacts in a single adsorbed step to CH_4, even though intermediate species $CHCl_3$, CH_2Cl_2, and CH_3Cl are almost unreactive.

Because of the multiplicity of reaction sites on a molecule with four chlorine atoms such as DDE, the entire reaction sequence to produce a chlorine-free biphenylethane must follow a network of concerted steps for olefinic chlorine removal and single steps for aromatic chlorine removal. This network was established quantitatively in the selectivity analysis of the system. The separate experiments with DDD, a 1,1-dichloroethane, confirmed that the process proceeds with DDE, a 1,1-dichloroethylene, first by chlorine removal. Only then does the olefin hydrogenate.

ACKNOWLEDGMENTS

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REFERENCES

1. Weiss, A. H., and Krieger, K. A., *J. Catal.* 6, 167–185 (1966).
2. Kammerer, H., Horner, L., and Beck, H., *Chem. Ber.* 91, 1376–1379 (1958).
3. Horner, L., Schlafer, L., and Kammerer, H., *Chem. Ber.* 92, 1700–1705 (1959).

4. Kraus, M., and Bazant, V., "Catalysis," Vol. 2, p. 1073. American Elsevier, New York, 1973.

5. Coulson, C. A., "Valence," 2nd ed., pp. 356–365. Oxford University Press, London, 1963.

6. Pauling, L., "The Nature of the Chemical Bond," 2nd ed. Cornell University Press, Ithaca, N. Y., 1945.

7. Morrison, R. T., and Boyd, R. N., "Organic Chemistry," 2nd ed., p. 826. Allyn and Bacon, Boston, 1966.

8. Gould, E. S., "Mechanism and Structure in Organic Chemistry," p. 216. Holt, Rinehardt, and Winston, New York, 1959.

9. LaPierre, R. B., Biron, E., Wu, D., Guczi, L., Kranich, W. L., and Weiss, A. H., "Catalytic Conversion of Hazardous and Toxic Chemicals: Pesticides and Related Substances," Document No. PB 262 804, EPA-600/3-77-018, January 1977. National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, Va. See also "Catalytic Hydrodechlorination of Polychlorinated Pesticides and Related Substances: An Executive Summary," EPA-600/8-77-013, September 1977.

10. Rylander, P. N., "Catalytic Hydrogenation over Platinum Metals," Chap. 24 (405). Academic Press, New York, 1967.

11. Amano, A., and Parravano, G., *Advan. Catal.* **9**, 717 (1957).

12. Kubicka, H., *J. Catal.* **12**, 223 (1968).

13. Anderson, J. R., "Structure of Metallic Catalysts," Chap. 2 (54). Academic Press, New York, 1975.

14. Wilke, C. R., and Lee, C. I., *Ind. Eng. Chem.* **47**, 1253 (1955).

15. Wilke, C. R., *Chem. Eng. Progr.* **46**, 95 (1950).

16. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," Chap. 1, pp. 44–45. M. I. T. Press, Cambridge, Mass., 1970.

17. Weisz, P. B., and Prater, C. D., *Advan. Catal.* **6**, 167 (1954).

18. Levenspiel, O., "Chemical Reaction Engineering," Chap. 9. Wiley, New York, 1964.

19. Wei, J., *Ind. Eng. Chem.* **58**, 38–44 (1966).

20. Beranek, L., *Advan. Catal.* **24**, 1 (1975).

21. Weiss, A. H., Gambhir, B., and Leon, R., *J. Catal.* **22**, 245-254 (1971).

22. Moyes, R. B., and Wells, P. B., *Advan. Catal.* **23**, 121 (1973).