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

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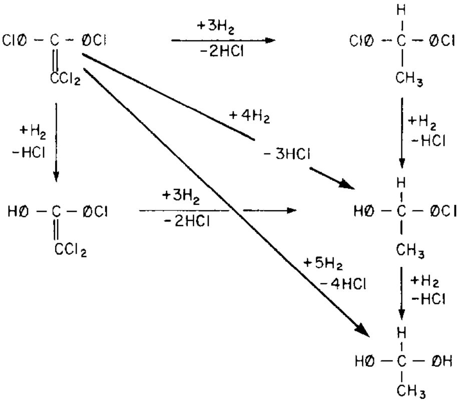
The liquid-phase catalytic hydrodechlorination of 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethylene (*p*,*p*′-DDE) was studied using 10% Pd on activated carbon and 61% Ni on kieselguhr catalysts. Reactions were carried out at temperatures of 20–100°C and hydrogen pressures from 1 to 50 atm. Ethanol was used as a solvent, and NaOH was used as an acid acceptor for the HCl by-product of the hydrodechlorination reactions. Both catalysts resulted in a complex network of reactions characterized by three paths: the removal of both olefinic chlorines followed by hydrogenation of the olefin, consecutive aromatic hydrodechlorination, and simultaneous occurrence of both of these paths. The steps involve as many as five molecules of hydrogen reacting without the observable desorption of intermediates.



(1)

Selectivity analysis by the reaction path method was used to determine the relative rates of each kinetic step in the above network. Absolute rate data are also provided.

INTRODUCTION

Several studies have been made of catalytic hydrodechlorination of chlorinated compounds according to the general reaction

$$R\text{–}Cl + H_2 \rightarrow R\text{–}H + HCl \quad (2)$$

The liquid phase reaction is usually carried out in the presence of an HCl acceptor such as NaOH dissolved in a polar solvent such as ethanol. The ease of reaction and the corresponding kinetics are strongly de-

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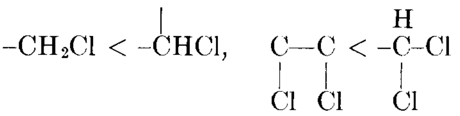
pendent on the structure of the carbon associated with the chlorine.

Transition metals have been used by Berg *et al.* (*1*) to remove halogen from organic substances. The metals were prepared in different forms (supported Pd and Pt, Pt black, and Raney nickel). High rates were achieved by Freifelder (*2*) using Pd on charcoal in the presence of an acid acceptor. He found that Raney nickel is also a good catalyst for hydrodechlorination, although nickel itself is not highly resistant to the HCl coproduct. By using an HCl acceptor, the effectiveness was improved, but still it was necessary to use large amounts of catalyst (50–300%).

Horner *et al.* (*3*) studied hydrodechlorination reactions for several types of halogen organics with Raney nickel. Their experiments resulted in a sequence of relative reactivities. They found that primary aliphatic chlorine is the least reactive, followed by secondary and vicinal halogens, then geminal halogens.



$$-CH_2Cl < -\overset{|}{C}HCl, \quad \underset{Cl}{\underset{|}{C}}-\underset{Cl}{\underset{|}{C}} < -\overset{H}{\underset{\underset{Cl}{|}}{C}}-Cl \qquad (3)$$

Kammerer *et al.* (*4*) used Raney nickel in the presence of alkali to hydrodechlorinate chlorobenzene.

Weiss and co-workers (*5–8*) studied the reactions of vinyl chloride, CCl_4, and *cis*- and *trans*-1,1-dichloroethylenes on a supported Pt catalyst. Reactivity increases in the sequence: aliphatic chlorine, vinyl chlorine, olefinic dichloride. Gas-phase 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethylene (*p,p′*-DDE) hydrodechlorination results (*9, 10*) supportive of the dichloroethylene work have recently been completed. Both *p,p′*-DDE and its corresponding ethane, *p,p′*-DDD, as 1% xylene solutions, were vaporized into 40- to 670-torr H_2 flowing over 0.35 wt% Pd on an α-Al_2O_3 catalyst. Reaction stoichiometry for DDE was a network characterized by addition of one H_2 to remove either one aromatic chlorine at a time or by the addition of three H_2 molecules, resulting in removal of two olefinic chlorides and olefin saturation. This latter occurred without any measurable intermediate desorption, a "concerted" step, behaving as one event. Previous work by Weiss and Krieger (*5*) on the lower molecular weight dichloroethylenes showed that first the olefinic chlorides are removed, and after that, the olefin is saturated. Weiss *et al.* (*6*) showed, in the case of CCl_4 hydrodechlorination, that CH_4 was produced in a single step, but the intermediates in this "concerted" addition of $4H_2$, $CHCl_3$, CH_2Cl_2, and CH_3Cl were quite unreactive.

Except for this present liquid-phase DDE work and the vapor-phase work on DDE, earlier hydrodechlorination investigations were concerned with organic compounds that each contained only one type of C–Cl bond. This study addresses the question of whether or not chlorine atoms bonded to different groups in a single molecule retain the relative reactivity as determined from studies of simple molecules. It is also concerned with the relative hydrodechlorination activity of polychlorinated compounds and to what extent DDT and DDE can be detoxified by a liquid-phase catalytic hydrodechlorination process, capable of removing chlorine to any desired extent.

EXPERIMENTAL

Hydrogen and nitrogen (both >99.9%) used for this study were obtained from Airco. Hydrogen was passed over copper to remove traces of oxygen. Both gas streams were dried over a bed of 5-A molecular sieves. Absolute ethanol was used as a solvent for the reaction. DDE was prepared by refluxing 0.01 *M* 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) (Montrose technical grade) in 0.05 *M* alcoholic NaOH for 16 hr. The recrystallized DDE product had a melting point of 87°C, and chromatographic analysis showed the crystals to be 99% *p,p′*-DDE and 1% of

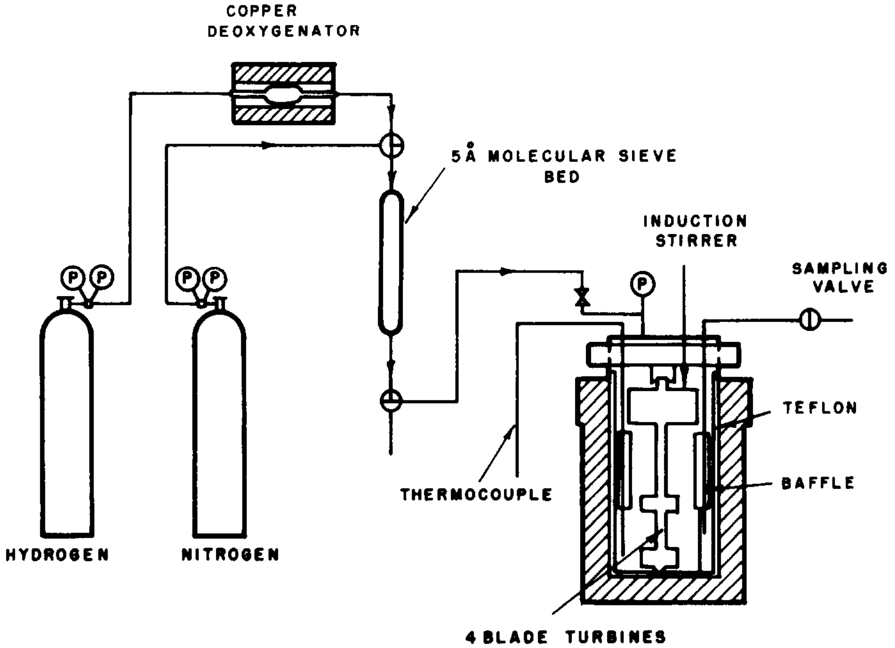


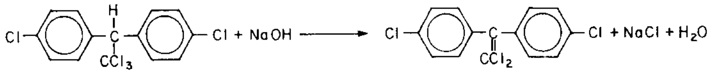
FIG. 1. Schematic of hydrodechlorination Teflon autoclave system.

the *o,p'*-DDE isomer. NaOH was Baker reagent grade. The catalysts employed in this study were Strem Chemicals Inc. 46-190 10% Pd on activated carbon and Girdler G-49A 61% Ni on kieselguhr. BET surface areas were 985 and 108 m^2/g, respectively. Both catalysts were finely powdered and had average particle sizes of less than 10 μm.

A modified 750-cm^3 stainless-steel Teflon-lined autoclave (Fig. 1) manufactured by Berghof GmBH was used for liquid-phase studies at elevated hydrogen pressure. The autoclave is equipped with a variable-speed induction-driven Teflon-coated stirrer. Two Teflon 1 × 0.5-in. four-blade turbine impellers were used to ensure good mixing characteristics. The first was located $\frac{1}{8}$ in. from the bottom of the Teflon liner to guard against settling of the slurried catalyst, while the second was located at the gas–liquid interface to optimize hydrogen mass transfer characteristics. The reactor also contained a $\frac{1}{16}$-in. sheathed iron constantan thermocouple and a $\frac{1}{16}$-in. stainless-steel high-pressure sampling tube, along with four $\frac{1}{8}$-in. cylindrical stainless-steel baffles. Corrosion or etching was not observed since excess NaOH was used as an acid acceptor. The reactant solutions of DDE and NaOH in ethanol were charged to the autoclave, and then reduced catalyst was added under nitrogen. The reactor was then sealed and purged several times with dry nitrogen and heated under nitrogen pressure. When the desired temperature was reached, the reactor was pressurized further with hydrogen, agitation at 1500 rpm was started, and this moment was recorded as the starting time of an experiment. Reaction temperatures ranged from 22 to 100°C, and hydrogen partial pressures ranged (P_{H_2}) from 5 to 50 atm, using reactor charges of 99 g of ethanol, 1.0 g of DDE, 0.553 g of NaOH, and 10–62.1 mg of Pd on carbon or 50 mg of Ni on kieselguhr catalyst.

The experiments made are applicable to DDT hydrodechlorination also. To illustrate this, one experiment is reported here using a conventional glass reactor at a

1-atm hydrogen pressure. In this particular experiment, 1.008 g of DDT was reacted in 100 ml of ethanol containing 0.7421 g of NaOH. To this was added 62.1 mg of 10% Pd on C activated at 220°C. By the time these procedures were accomplished, the HCl elimination reaction (dehydrochlorination) at room temperature (23°C) had effectively converted all of the DDT to DDE:


(VI)

(4)

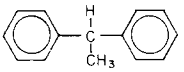
The reaction mixture contained only DDE and was then studied as catalytic DDE hydrodechlorination at 23°C.

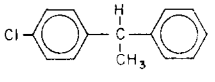
Gas chromatography–mass spectroscopy (GC–MS) techniques provided quantitative identification of all reactants and products. The equipment used was a Perkin–Elmer Model 900 dual flame ionization detector gas chromatograph interfaced with a DuPont 21-491 double-focusing mass spectrometer. Chromatographic separations were carried out on a 3-m × $\frac{1}{8}$-in. 3% OV.17 on 80–100 mesh Chromosorb W-HP column. Helium flow rate was 30 cm^3/min, and the column was temperature-programmed from 152 to 250°C at ca. 5°C/min. Data reduction was carried out on a Columbia Scientific Industries CSI-20B automatic digital integrator. Further analytical details are in (*10*). Based on the correlation of Wilke and Chang (*11*), the bulk diffusivity of DDE in ethanol was calculated to be $\approx 10^{-5}$ cm^2/sec at 60°C. Using the calculation procedure of Satterfield (*12*), it was shown that there were no bulk mass transfer limitations. Reducing stirrer speed from 1500 to 900 rpm in one test had no effect on intermediate selectivities or DDE conversion at 50 atm of H_2 and 60°C (Table 1).

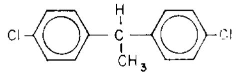
By assuming that the effective pore diffusivities of DDE were two orders of magnitude lower than the bulk value, Weisz and Prater's (*13*) criterion for surface reaction control was calculated. All observed DDE reaction rates were in the surface-controlled regime.

RESULTS

Three major DDE (VI) hydrodechlorination products were observed in both the Ni and Pd catalyzed systems:

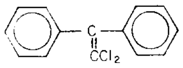

(I)

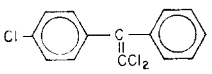

(II)


(III)

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

Aromatic hydrodechlorination products where the olefinic chlorines were unreacted were almost undetectable


(IV)


(V)

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

These were present in significant quantities in gas-phase studies of DDE hydrodechlorination over 0.35 wt% Pd on α-Al_2O_3 (*9, 10*). Small amounts of diphenylethylenes containing no, one, and two aromatic chlorines were observed at low conversion. 2-Chloro-1,1-diphenylethylenes/ethanes were also present in trace amounts. Oligomerization and ring saturation were not significant side reactions.

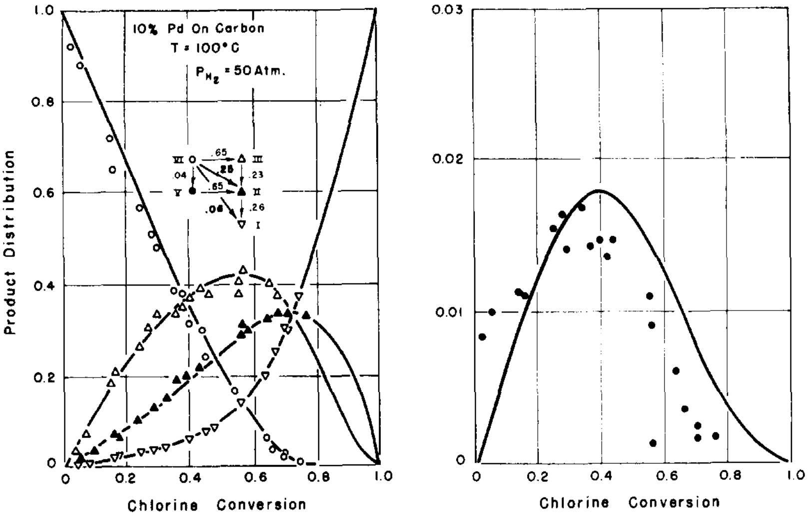


FIG. 2. DDE hydrodechlorination reaction paths over 10% Pd on carbon at 100°C, 50 atm of H_2. Selectivity curves calculated using the indicated first-order relative rate constants.

Chlorine conversion was used as an extent-of-reaction parameter and is defined as $(4 - \phi)/4$, where

$$\phi = \sum_{h=1}^{4} h\text{Cl}_h, \tag{5}$$

4 = number of chlorine atoms per reactant molecule,

h = number of chlorine atoms per molecule,

and

Cl_h = relative mole fraction of compounds with h chlorine atoms per molecule.

Figure 2 shows a typical selectivity plot (i.e., product distribution vs chlorine conversion) for the DDE hydrodechlorination over 10% Pd on carbon at 100°C, 50 atm of H_2. The product distribution can be

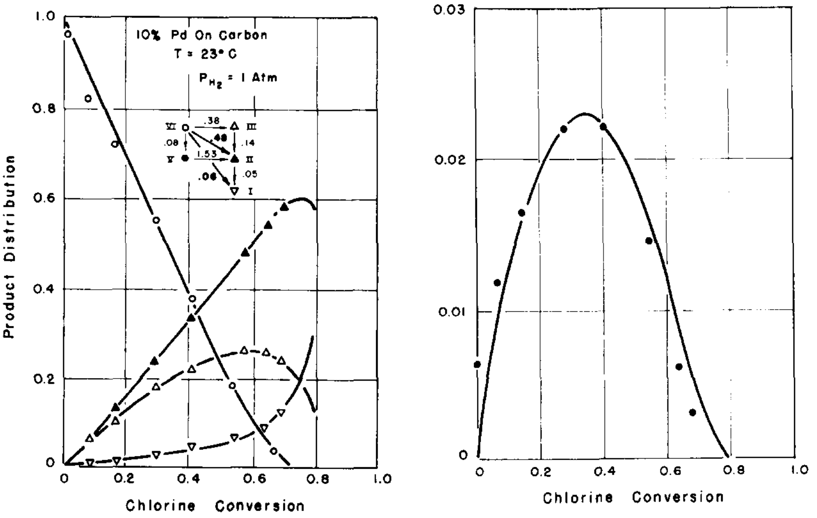


FIG. 3. DDE (ex-DDT + NaOH in ethanol) hydrodechlorination reaction paths over 10% Pd on carbon at 23°C, 1 atm of H_2. Selectivity curves calculated using the indicated first-order relative rate constants.

TABLE 1

Pd-Catalyzed Hydrodechlorination: Relative Rate Constants[a]

Temperature (°C)	P_{H_2} (atm)	k'_{65}	k'_{63}	k'_{62}	k'_{61}	k'_{52}	k'_{32}	k'_{21}
100[b]	50	0.04	0.80	0.14	0.02	—[c]	—[c]	—[c]
100	50	0.04	0.65	0.25	0.06	0.65	0.23	0.26
100[d]	50	0.04	0.65	0.25	0.06	0.65	0.23	0.26
80.5	50	0.04	0.80	0.14	0.02	0.80	0.06	0.04
81.5	50	0.04	0.80	0.14	0.02	0.80	0.06	0.04
60	50	0.04	0.75	0.17	0.04	0.75	0.17	0.13
60	50	0.04	0.82	0.12	0.02	0.82	—[c]	—[c]
59.5[e]	50	0.04	0.82	0.12	0.02	0.82	—[c]	—[c]
24–47	50	0.03	0.83	0.09	0.05	—[c]	—[c]	—[c]
98	20	0.05	0.64	0.26	0.05	0.64	0.20	0.14
24–47	20	0.05	0.69	0.22	0.04	—[c]	—[c]	—[c]
100	7	0.07	0.53	0.30	0.10	0.72	0.38	0.27
22–42	5	0.07	0.54	0.30	0.09	1.60	0.15	0.10
23	1	0.08	0.38	0.48	0.06	1.53	0.14	0.05

[a] Catalyst, 10% Pd on carbon; reduction temperature, 220°C; stirrer speed, 1500 rpm; catalyst loading, 0.24 g/liter; DDE concentration, 2.53 × 10^{-2} *M*.

[b] Catalyst concentration, 0.08 g of catalyst/liter.

[c] Insufficient data.

[d] Catalyst concentration, 0.16 g of catalyst/liter.

[e] Stirrer speed, 900 rpm.

compared to that plotted on Fig. 3 for the just-mentioned DDT experiment at the other extreme of reaction conditions studied, 23°C, 1 atm of H_2. Intermediate reaction conditions (listed in Table 1) gave a similar degree of correlation to the calculated curves on Figs. 2 and 3.

Figure 4 is a selectivity chart for the 61% Ni on kieselguhr catalyst studied. Not only does it provide a comparison between

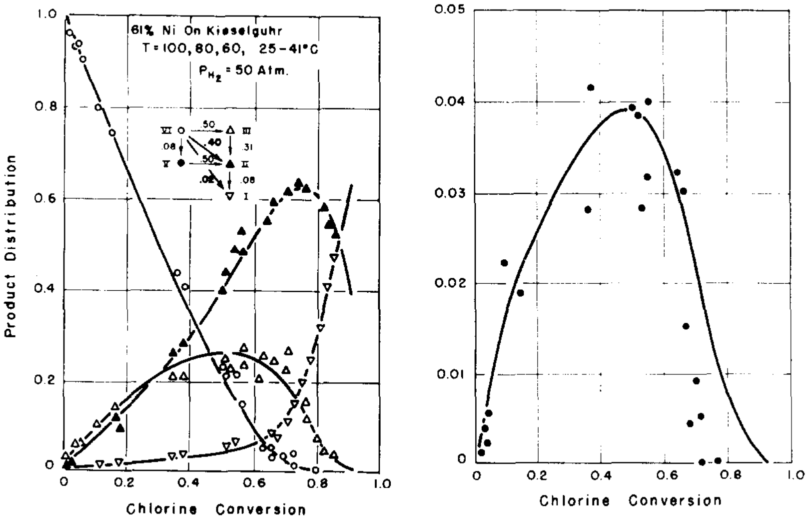
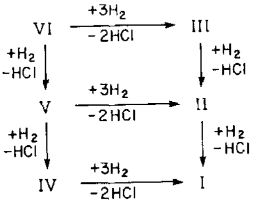


FIG. 4. DDE hydrodechlorination over 61% Ni on kieselguhr catalyst at 50 atm of H_2 and 25 to 100°C. Selectivity curves calculated using the indicated first-order relative rate constants.

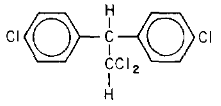
Ni and Pd (Fig. 2) at 50 atm, but because of the fit of all data points from 27 to 100°C to the calculated curves, it illustrates that there are no significant activation energy differences in the removal of any particular DDE chlorine.

In the gas phase (*9*, *10*), the observed reaction network that fitted the experimentally observed product distributions was as follows:



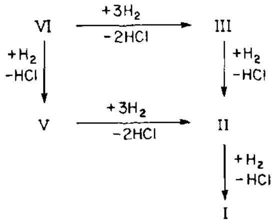
(6)

Similar to the gas-phase experiments, both Ni and Pd showed removal of both olefinic chlorines along with hydrogenation of the resulting olefin to ethane in a concerted process. Only small amounts of V were measured (see Figs. 2, 3, and 4). (Species IV was present in immeasurably small amounts in the liquid phase.) Hydrogenation of the double bond of VI to



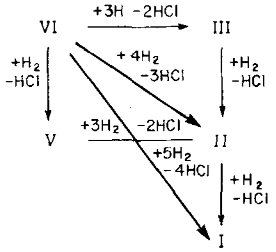
1,1-bis(*p*-chlorophenyl)-2,2-dichloroethane (*p,p'*-DDD), was not observed, indicating that, as in the gas phase, olefinic hydrodechlorination is a precursor to hydrogenation of the double bond.

Since IV was immeasurable, we originally believed that we could approximate the kinetics by a simpler scheme for the liquid phase than for the gas phase:



(7)

However, there was no way to accommodate the experimental results to such a model, as can be seen by the finite initial slope of the curves in Figs. 2–4 for species II, and to a lesser extent for species I. Additional concerted pathways directly from species VI to II and VI to I must be included in the liquid-phase reaction network, since species II and I appear as initial products.[4] These are shown boldface below:



(8)

The significance of such a reaction network is that as many as five hydrogen molecules react with DDE in one concerted step to produce biphenyl ethane, without DDE or an intermediate ever leaving the catalyst site. This is quite analogous to the concerted hydrodechlorination behavior reported by Weiss *et al.* (*6*) for Pt-catalyzed CCl_4 hydrodechlorination:

$$\begin{tikzcd}
CCl_4 \arrow[r, "+4H_2", "-4HCl"'] \arrow[d, "+H_2"', "-HCl"] & CH_4 \\
CHCl_3 &
\end{tikzcd} \qquad (9)$$

In the case of CCl_4, the expected intermediates $CHCl_3$, CH_2Cl_2, and CH_3Cl are effectively unreactive, so concerted hydrodechlorination is not a case of strongly adsorbed *reactive* intermediates. The lack of these steps in the gas-phase work (*9*) may be due to the presence of a large excess of *p*-xylene in the feed which inhibited

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[4] Observe the finite slopes for II and I on Figs. 2–4. If these species were produced *only* as a result of consecutive reactions, the initial slopes would be zero.

TABLE 2

Ni-Catalyzed Hydrodechlorination: Relative Rate Constants[a]

Temperature (°C)	Catalyst reduction temperature (°C)	k'_{65}	k'_{63}	k'_{62}	k'_{61}	k'_{52}	k'_{32}	k'_{21}
100	370	0.08	0.50	0.40	0.02	0.50	0.31	0.08
80	370							
60	370							
25–41	370							
99	220	0.06	0.64	0.27	0.03	0.64	0.12	0.05
60.5	220							
81.5	220	0.06	0.76	0.17	0.01	0.76	0.05	0.025
27–42	220							

[a] Catalyst, 61% Ni on kieselguhr; stirrer speed, 1500 rpm; catalyst loading, 0.40 g/liter; DDE concentration, $2.53 \times 10^{-2}\,M$; P_{H_2} 50 atm.

multipoint adsorption of DDE. Liquid-phase experiments with *p*-xylene as a solvent, $Ca(OH)_2$ or $Na(OH)$ as acid acceptor, and the Ni on kieselguhr catalyst were attempted. However, only trace amounts of the completely hydrodechlorinated product 1,1-diphenylethane were formed, most likely as the consequence of insolubility of the acid acceptor in the xylene.

The first-order reaction paths that correspond to the stoichiometry of this reaction set (7) are described by the following set of normalized first-order differential equations which simulate batch reaction behavior, where A_i is the liquid phase concentration of species i, and, by definition, the sum

$$(k'_{65} + k'_{63} + k'_{62} + k'_{61}) = 1. \quad (10)$$

$$\frac{dA_{\mathrm{V}}}{dA_{\mathrm{VI}}} = \frac{k'_{65}A_{\mathrm{VI}} - k'_{52}A_{\mathrm{V}}}{-(k'_{65} + k'_{63} + k'_{62} + k'_{61})A_{\mathrm{VI}}} \quad (11)$$

$$\frac{dA_{\mathrm{III}}}{dA_{\mathrm{VI}}} = \frac{k'_{63}A_{\mathrm{VI}} - k'_{32}A_{\mathrm{III}}}{-(k'_{65} + k'_{63} + k'_{62} + k'_{61})A_{\mathrm{VI}}} \quad (12)$$

$$\frac{dA_{\mathrm{II}}}{dA_{\mathrm{VI}}} = \frac{k'_{62}A_{\mathrm{VI}} + k'_{52}A_{\mathrm{V}} + k'_{32}A_{\mathrm{III}} - k'_{21}A_{\mathrm{II}}}{-(k'_{65} + k'_{63} + k'_{62} + k'_{61})A_{\mathrm{VI}}} \quad (13)$$

$$\frac{dA_{\mathrm{I}}}{dA_{\mathrm{VI}}} = \frac{k'_{61}A_{\mathrm{VI}} + k'_{21}A_{\mathrm{II}}}{-(k'_{65} + k'_{63} + k'_{62} + k'_{61})A_{\mathrm{VI}}} \quad (14)$$

We define, k'_{ij} as pseudohomogeneous relative rate constants of the form $k_{ij}\ K_i\ P_{H_2}{}^{n \text{ or } m}$. This was discussed previously (*9*) where k_{ij} = intrinsic rate constant to produce species j from species i by hydrodechlorination, K_i = adsorption equilibrium constant for species i, and n or m = order in H_2 for aromatic or olefinic chlorine removal, respectively. For the following selectivity analysis in which only relative rate constants are treated, it is not necessary to consider Langmuir–Hinshelwood surface terms in the rate constants, since they cancel when rate constants k_{ij} are divided to define relative rate constants. That is, all species see the same surface.

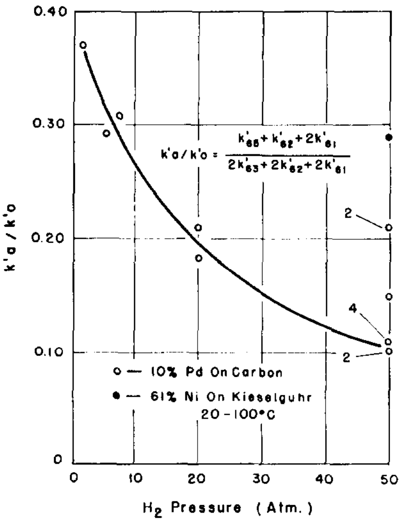

FIG. 5. The ratio k'_a/k'_0, an indicator of the ratio of aromatic to olefinic hydrodechlorination, decreases with increasing hydrogen partial pressure.

These values of k'_{ij} have been calculated from the experimental product distributions of this study. Figures 2–4 are typical fits of experimental data to the calculated first-order reaction paths that correspond to the indicated k'_{ij} values. The operating conditions and values of k'_{ij} for all of the conditions studied for 10% Pd on C catalyst are listed in Table 1. Those for 61% Ni on kieselguhr catalyst are in Table 2.

Table 1 shows that for the Pd-catalyzed experiments the values of k'_{62} and k'_{61} which characterize the concerted simultaneous removal of aromatic and olefinic chlorine increase with decreasing P_{H_2}. Since absolute rates decrease with decreasing P_{H_2}, this trend is just the opposite of that expected if the concerted behavior were a result of pore diffusion limitations. Concerted bebehavior is most likely the result of fast reaction and very slow desorption of intermediates (whatever they might be in this case) as discussed by Beranek (*14*). The value of k'_{65} (which characterizes DDE aromatic hydrodechlorination) increases with decreasing P_{H_2}, as was observed in the gas-phase studies (*9*, *10*). However, the values of k'_{32} and k'_{21} [which characterize the hydrodechlorination of the 1,1-bis-(*p*-chlorophenyl)ethane] showed no consistent trend but varied randomly.

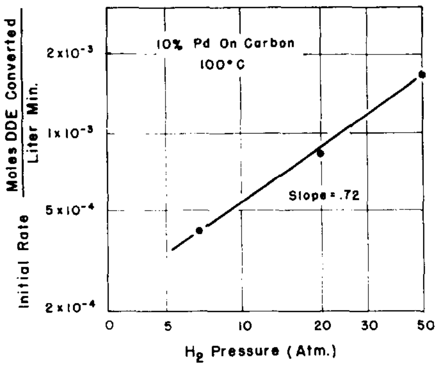

FIG. 6. Initial DDE conversion rates are fitted to 0.72 order in hydrogen.

Table 2 shows that for the Ni-catalyzed experiments the reduction temperature of the catalyst had a significant effect on selectivities and associated relative rate constants. The ratio

$$\frac{k'_a}{k'_0} = \frac{k'_{65} + k'_{62} + 2k'_{61}}{2k'_{63} + 2k'_{62} + 2k'_{61}} \tag{15}$$

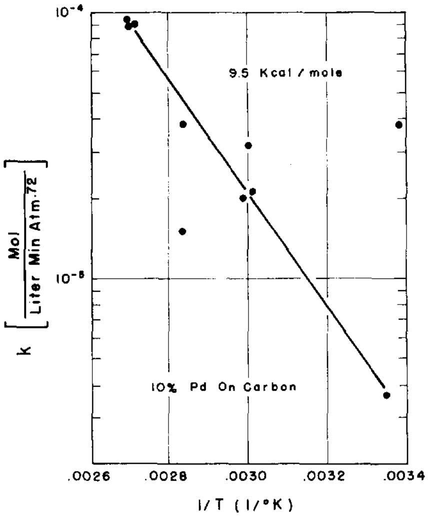

FIG. 7. When DDE hydrodechlorination initial rates are fitted by kinetics that are zero order in DDE and 0.72 order hydrogen, activation energy = 9.5 kcal/mol for 10% Pd on carbon catalyst.

defines the relative rate constant ratio of aromatic to olefinic chlorine removal. The numerical coefficients account for the number of chlorine atoms removed in that particular reaction step from the aromatic or olefin position. This ratio, which is an indicator of aromatic to olefinic chlorine hydrodechlorination selectivity, is plotted in Fig. 5 as a function of P_{H_2}. In the case of 10% Pd on C catalyst, it decreases from 0.37 to as low as 0.10 when P_{H_2} varies from 1 to 50 atm. The results for Ni on kieselguhr catalyst on Fig. 5 at 50 atm show that Ni is intrinsically more selective to aromatic hydrodechlorination than is Pd on carbon: $-k'_a/k'_0 = 0.30$ vs 0.10 to 0.22, respectively.

Experiments were made at 50, 20 and 7 atm of H_2, respectively, 100°C, and a Pd catalyst concentration of 0.242 g/liter to determine the effect of H_2 pressure on the initial reaction rate. Figure 6 is a log-log plot of initial DDE conversion rate vs H_2 pressure which gave a +0.72-order H_2 dependence. The initial rates of all other Pd-catalyzed experiments were divided by $P_{H_2}{}^{0.72}$ to determine the apparent activation energy for DDE reaction. Order of magnitude variances in the initial rates obtained at room temperature were observed but cannot be explained. Figure 7 is an Arrhenius plot for these experiments which gave a value of E = 9.5 kcal/mole for Pd on carbon.

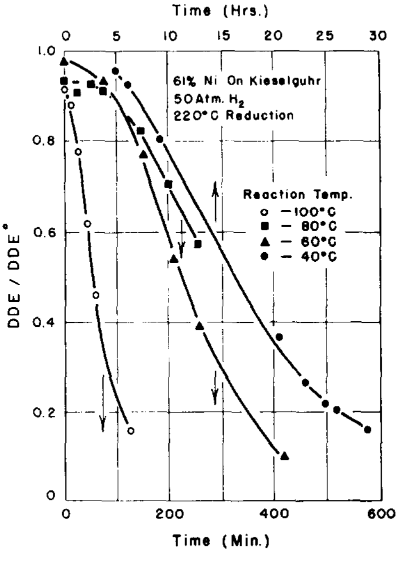

FIG. 8. DDE fractional conversion vs time for 61% Ni on kieselguhr catalyst reduced at 220°C.

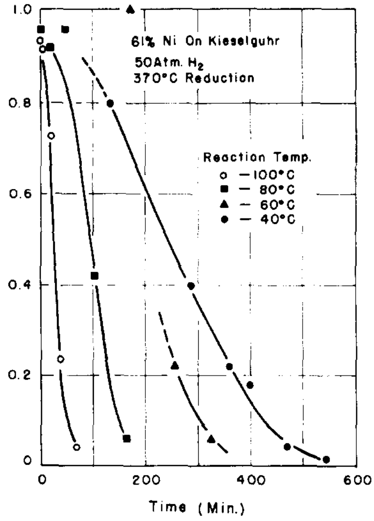

FIG. 9. DDE fractional conversion vs time for 61% Ni on kieselguhr catalyst reduced at 370°C.

The kinetic behavior of Ni-catalyzed DDE hydrodechlorination is quite different from that observed in the Pd-catalyzed experiments. Although the overall behavior can be satisfactorily represented by the first-order treatment used in Fig. 4, in detail DDE concentration vs time curves, plotted on Figs. 8 and 9, are characterized by three regimes: (i) an induction period; (ii) zero-order behavior at intermediate conversions; and (iii) a shift to higher order functionality at high conversions. The G-49-A 61% Ni on kieselguhr catalyst is prereduced and stabilized by the manufacturer. However, Ni on SiO_2 catalysts are notoriously difficult to reduce. In these experiments two reduction temperatures, 220 and 370°C, were utilized. Figures 8 and 9 are relative DDE concentration vs time plots for experiments conducted at 50 atm of H_2 and temperatures from 40 to 100°C. Reduction temperatures are, respectively, 220 and 370°C. In both sets of

TABLE 3

Induction Periods Observed for 61% Ni on Kieselguhr Catalysts

Reaction temperature (°C)	Induction period (min)	
	220°C reduction	370°C reduction
40	225	60
60	75	—
80	75	35
100	6	<5

TABLE 4

Rates Using Ni Catalyst Reduced at 370°C

Temperature (°C)	P_{H_2} (atm)	Zero-order DDE rate (mol/liter-min)
100	50	7.44×10^{-4}
80	50	2.94×10^{-4}
40	50	6.84×10^{-5}

experiments, the length of the induction period decreases as reaction temperature increases (see Table 3).

Increasing reduction temperature decreases the length of the induction period. The induction period observed with Ni catalyst could be due either to continuing *in situ* reduction of the catalyst as reaction proceeds or to poisoning by products or reactants. Lack of this induction period in the Pd-catalyzed experiments rules out the possibility of this effect being due to slow saturation of the liquid phase with hydrogen after the reactor was pressurized.

Zero-order behavior (i.e., DDE conversion vs time) at intermediate conversions is probably an indication that DDE is more strongly adsorbed on Ni than on Pd. The higher degree of concerted behavior at similar conditions is consistent with this observation, as the possibility of multiple reaction steps occurring with a more strongly adsorbed substrate is favored.

At higher conversions a shift to higher order kinetics was observed. This type of behavior is expected for systems that obey Langmuir–Hinshelwood rate expressions as the surface concentration of strongly adsorbed reactants approaches zero. The apparent activation energy for the Ni-catalyzed experiments where the catalyst was reduced at 370°C was determined from the zero-order portion of the concentration vs time curves (see Table 4). These values yielded an apparent activation energy of $E = 9.3$ kcal/mol (Fig. 10), comparable to the 9.5 kcal/mol obtained for the Pd-catalyzed experiments.

DISCUSSION AND CONCLUSIONS

We have previously reported (*5*, *9*) that the catalytic activity of aromatic and olefinic chlorine is due to the distinct double-bond character of the carbon–chlorine bond as the chlorine atom loses π electrons, $>\overset{\delta^-}{C}\!\!=\!\!\overset{\delta^+}{Cl}$ (*15*). Those types of chlorine which undergo hyperconjugation readily are more catalytically reactive than aliphatic chlorine, as has been shown previ-

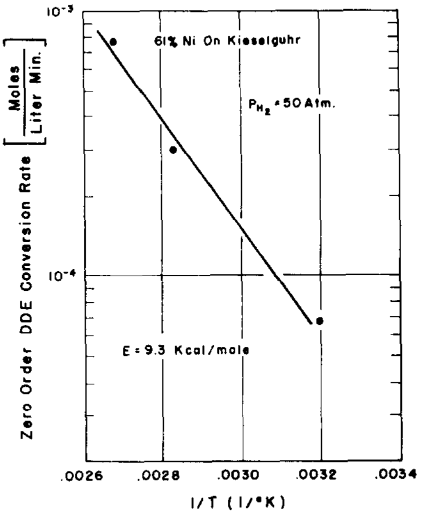

FIG. 10. When DDE hydrodechlorination rates are fitted (after the induction period) by kinetics that are zero order in DDE at a constant $P_{H_2} = 50$ atm, activation energy = 9.3 kcal/mol for 61% Ni on kieselguhr catalyst.

ously for other molecules (*5*). In this study we have shown that the stoichiometry and selectivity for both Pd and Ni-catalyzed liquid-phase DDE hydrodechlorination are similar. The major difference in behavior in liquid phase with ethanol as solvent from that in the gas phase in the presence of excess *p*-xylene is that the concerted simultaneous removal of aromatic and olefinic chlorine from the same substrate occurs to a much greater extent. This concerted behavior, in which as many as 5 mol of H_2 react with DDE without measurable desorption of intermediates is, as might be expected, related to hydrogen partial pressure.

The selectivity analysis suggests that, although the DDE molecule is roughly planar, there are three major possible, but unproven, adsorbed states of DDE in these liquid-phase studies: (i) aromatic moiety-adsorbed (k'_{65}, k'_{32}, k'_{21}); (ii) aromatic and olefinic moieties-adsorbed (k'_{62}, k'_{61}); and (iii) olefinic moiety-adsorbed (k'_{63}, k'_{52}). In the gas-phase studies (*9, 10*), k'_{62} and k'_{61} were zero, implying that either the aromatic or olefinic moiety alone was adsorbed, but not the two together. This is most likely a consequence of the presence of a strongly adsorbed inhibitor, *p*-xylene, which competed for the catalytic surface.

Hydrogen availability (i.e., high partial pressure) affects the observed degree of concerted multistep vs nonconcerted single-step behavior in an ethanol–NaOH solution. As in the gas-phase studies, olefinic hydrodechlorination is more hydrogen-pressure-dependent than aromatic hydrodechlorination.

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