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Hydrodechlorination of Polychlorinated Biphenyl

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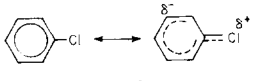
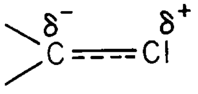
The catalytic hydrodechlorination of a complex polychlorinated biphenyl (PCB) mixture was studied in a batch reactor using a 61% Ni on kieselguhr catalyst from 25 to 100°C at 50 atm of H_2. Ethanol was used as a solvent and NaOH as an acid acceptor. Aromatic hydrodechlorination of chlorinated biphenyls is a consecutive single-step process; *ortho*-substituted chlorine is the least labile due to steric effects. In the reaction sequence below, $\phi\phi_i$ indicates a biphenyl molecule substituted with i chlorine atoms distributed over the two rings. First-order pseudo-homogeneous relative rate constants for the liquid phase study are noted:

$$\phi\phi_5 \xrightarrow{1} \phi\phi_4 \xrightarrow{0.40} \phi\phi_3 \xrightarrow{0.23} \phi\phi_2 \xrightarrow{0.36} \phi\phi_1 \xrightarrow{0.40} \phi\phi_0$$

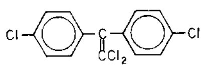
Similar behavior was observed in a gas-phase pulse microreactor over a series of 0.00, 0.05, 0.10, and 0.35 wt% Pd on α-Al_2O_3 catalysts at 220 ± 5°C, 2.3 atm of H_2, and space time of $\sim 10^{-2}$ sec (based on H_2 carrier gas flow rate). The corresponding values of the relative rate constants were 1.0, 0.85, 0.50, 0.70, and 0.95. These values of relative rate constants pass through a minimum as a result of the combined influence of statistical and steric factors. Highly *ortho*-substituted materials cannot adsorb in a planar configuration. The relative first-order rate constant for *ortho* to (*meta* + *para*) hydrodechlorination (k_o/k_{mp}) = 0.52 for the nickel catalyst. Reaction behavior is consistent with the mechanism requiring adsorption of the benzene ring and charge delocalization at the aromatic chlorine:



For hydrodechlorination, the  carbon–chlorine double bond is regarded as the reactive species.

INTRODUCTION

We have recently reported (*1*, *2*) on the stoichiometry and kinetics of the gas- and liquid-phase hydrodechlorination of *p,p'*-DDE (1,1-bis(*p*-chlorophenyl)-2,2-dichloroethylene):



In this study we present liquid-phase hydrodechlorination results on a related high molecular weight class of compounds, polychlorinated biphenyls (PCBs). The

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reaction proceeds in ethanol in the presence of a NaOH acid acceptor.

Gas-phase hydrodechlorination of PCB to completely hydrodechlorinated species has been described earlier (*3*, *4*). Berg *et al.* (*4*) reported virtually quantitative hydrodechlorination of PCB at 180°C using 5% Pt or Pd on glass as a catalyst. They established a technique for identifying PCB in a mixture of organochlorine pesticides. Recently, an extensive review of PCB chemistry has been published by Hutzinger *et al.* (*5*). Other reviews of hydrodechlorination literature and associated mechanisms have been presented by us elsewhere (*1*, *2*, *6*).

EXPERIMENTAL

The reactant used in these studies was Monsanto Aroclor 1248, a clear, viscous oil containing 48% chlorine by weight. This corresponds to an average of 3.92 chlorine atoms per biphenyl molecule. Hydrogen and nitrogen (both > 99.9%) were obtained from Airco. The solvent used was absolute ethanol, and the acid acceptor was NaOH (Baker reagent grade). The catalyst used was Girdler G49-A, 61% Ni on kieselguhr with a N_2 BET surface area of 108 m^2/g.

Reactions were carried out in a Teflon-lined autoclave (Berghof GmBH) in a conventional system. A detailed description of the equipment, operating procedures used, and mass transfer characteristics is in (*2*).

In the liquid-phase experiments of this study, 100 g of 2 wt% Aroclor 1248 in ethanol was reacted at 50 atm of H_2 pressure with 200 mg of Girdler G49-A and with 110% of the NaOH required to neutralize all HCl produced by complete hydrodechlorination. The experiments were conducted at 60, 80, 100, and 130°C, respectively, and the reactor was sampled periodically. The pulse microreactor used for the gas-phase experiments was the inlet of a Perkin–Elmer Model 900 gas chromatograph. In the pulse experiments, differential beds of a series of 0.00, 0.05, 0.10, and 0.35 wt% Pd on α-Al_2O_3 catalysts (Girdler Catalyst Corp.) were used to obtain selectivity data at 220 ± 5°C and 2.3 atm of H_2 pressure. Normal heptane was used as a solvent for the Aroclor 1248. Space time was 0.01 sec based on H_2 carrier gas flow rate.

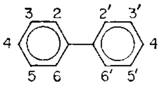
Gas chromatography–mass spectroscopy (GC–MS) techniques were used for identification and quantitative analysis of all reactants and products. Analytical equipment included a Perkin–Elmer Model 900 dual flame ionization detector (FID) gas chromatograph interfaced with a DuPont 21-491 double-focusing mass spectrometer. A CSI Model 208 automatic digital integrator was used for quantitating FID output. Mass spectra were recorded using a CSI 5-124A recording oscillograph. Molecular weight determination and structural information obtained from the mass spectra of individual chromatographic peaks identified reaction intermediates in the complex system studied. The carbon-counting flame ionization detector gave quantitative conversion and rate data on a mole fraction basis.

The linearity of the FID response was confirmed for both biphenyl and Aroclor 1248 up to 0.3- and 0.15-μmol levels, respectively, even though column overloading was observed at the largest sample sizes. Analysis of Aroclor 1248 reaction products was carried out at the 0.076-μmol level, well within the linear range of the analysis.

Reactants and products were separated on a 9-ft × $\frac{1}{8}$-in. 3% OV-17 Chromosorb W-HP column which could be operated up to 250°C without significant column bleed. A 6-ft × $\frac{1}{8}$-in. 3% SE-30 on Chromosorb W-HP column was used to reproduce the results of Webb and McCall (*7*), who used a 100-ft × 0.02-in. SE-30 Scot Column for identification of individual PCB isomers.

The mass spectra of a number of individual isomeric chlorobiphenyls (PCBs) have been summarized by Safe and Hutzinger (*8*). In general, the electron ionization mass spectra of PCBs are characterized by intense molecular ions and elimination of two chlorine atoms from biphenyl containing two or more chlorine atoms per molecule. The primary ion mass spectra of isomeric species are virtually identical except that highly *ortho*-substituted PCB gives more intense *m/e*-70 fragments.

Figure 1 is an OV-17 chromatogram of the Aroclor 1248 with the number of chlorines per molecule identified by the observed molecular ions. Break points between groups of peaks containing the same number of chlorine atoms per molecule were selected accordingly, although some overlap was observed. Table 1 lists retention time, number of chlorine atoms per molecule identified by GC–MS, and relative mole fraction of each peak in the Aroclor 1248. The commonly accepted nomenclature for PCB is as follows:



It is the practice to name 2, 2′, 6, and 6′ positions as *ortho*; 3, 3′, 5 and 5′ positions as *meta*; and 4 and 4′ positions as *para*. The procedure of Webb *et al.* on SE-30 gave isomer distributions for Aroclor 1248 almost identical to the following total values that were obtained by us with OV-17 on the sample used for this work: *o*-chlorine, 1.68; *m*- + *p*-chlorine, 2.24; total chlorine, 3.92. The analysis shown in Table 1 and totaled in Table 2 corresponds to an average of 3.925 chlorine atoms/molecule or an average molecular weight of 289.2 ($C_{12}H_{6.075}Cl_{3.925}$) as compared to the 3.90 and 288 figures reported by Hutzinger (*5*). For convenience, we shall designate a biphenyl molecule substituted with i chlorine atoms as $\phi\phi_i$. Table 2 lists the total number of PCB isomers, calculated by Smith (*9*), and the distribution of the Aroclor 1248 used here.

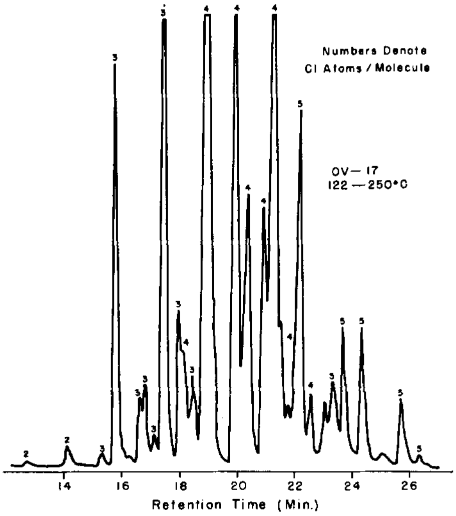


FIG. 1. Aroclor 1248 gas chromatogram. The numbers on each peak indicate the number of Cl atoms per molecule.

RESULTS

Figure 2 is a plot of the relative mole fraction of each species $\phi\phi_i$ vs chlorine conversion, X, for the liquid-phase Ni-catalyzed work. Chlorine conversion is used as an extent-of-reaction parameter and is defined as:

$$X = 1 - \sum_{i=0}^{5} i\phi\phi_i / \sum_{i=0}^{5} i\phi\phi^{\circ},$$

where $\phi\phi_i$ = mole fraction of biphenyl species containing i chlorine atoms per molecule, and superscript o refers to the initial distribution.

These observed selectivity data are described by a pseudohomogeneous consecutive reaction scheme

$$\phi\phi_5 \xrightarrow{k'_{54}} \phi\phi_4 \xrightarrow{k'_{43}} \phi\phi_3 \xrightarrow{k'_{32}} \phi\phi_2 \xrightarrow{k'_{21}} \phi\phi_1 \xrightarrow{k'_{10}} \phi\phi_0,$$

TABLE 1

Aroclor 1248 GC–MS Analysis[a]

Retention time (min)	Cl atoms per molecule	Mole fraction
5.0	0	
6.8	0	
9.8	1	0.0009
11.2	1	
11.3	1	
12.4	2	0.0015
13.0	2	
13.5	2	0.0052
13.8	2	
15.1	3	0.0025
15.7	3	0.0658
16.2	3	0.0021
16.5	3	0.0099
16.7	3	0.0144
17.0	3	0.0054
17.4	3	0.0993
17.9	3	0.0422
18.4	3	0.0177
18.8	4	0.1768
19.1	4	
20.0	4	0.0926
20.4	4	0.0625
20.9	4	0.0470
21.3	4	0.1446
21.8	4	0.0086
22.3	5	0.0785
22.6	5	0.0130
23.1	5	0.0131
23.4	5	0.0209
23.7	5	0.0283
24.4	5	0.0274
25.0	5	0.0035
25.7	5	0.0131
26.1	5	0.0031

[a] Column, 9 ft × ⅛ in, 3% OV-17 on Chromosorb W; 30 ml/min of He; 122–250°C at 5°C/min.

where each k'_{ij} is the product of an intrinsic rate constant k_{ij} and an adsorption equilibrium constant K_i. In the selectivity analysis to follow (in which rate constant ratios are used), any Langmuir–Hinshelwood surface terms that might be in the rate law will cancel, since, in this system, all species see the same surface. The set of first-order reaction path expressions which describe the system is as follows:

$$\frac{d\phi\phi_4}{d\phi\phi_5} = \frac{k'_{43}\phi\phi_4}{k'_{54}\phi\phi_5} - 1$$

$$\frac{d\phi\phi_3}{d\phi\phi_5} = -\left(\frac{k'_{43}\phi\phi_4 - k'_{32}\phi\phi_3}{k'_{54}\phi\phi_5}\right)$$

$$\frac{d\phi\phi_2}{d\phi\phi_5} = -\left(\frac{k'_{32}\phi\phi_3 - k'_{21}\phi\phi_2}{k'_{54}\phi\phi_5}\right)$$

$$\frac{d\phi\phi_1}{d\phi\phi_5} = -\left(\frac{k'_{21}\phi\phi_2 - k'_{10}\phi\phi_1}{k'_{54}\phi\phi_5}\right)$$

$$\frac{d\phi\phi_0}{d\phi\phi_5} = -\frac{k'_{10}\phi\phi_1}{k'_{54}\phi\phi_5}$$

The best fit was obtained with the following set of relative rate constants:

$\frac{k'_{43}}{k'_{54}}$	$\frac{k'_{32}}{k'_{54}}$	$\frac{k'_{21}}{k'_{54}}$	$\frac{k'_{10}}{k'_{54}}$
0.40	0.23	0.36	0.40

The curves calculated by using this set of constants are superimposed on the data in Fig. 2. Since the data for the entire temperature range fit a single reaction path for a given species, it can be concluded

TABLE 2

PCB Isomers for Each Aroclor Homolog

$\phi\phi_i$	No. of isomers	Aroclor 1248 mole fraction
0	1	
1	3	0.0009
2	12	0.0067
3	24	0.2593
4	42	0.5321
5	46	0.2009
6	42	
7	24	
8	12	
9	3	
10	1	

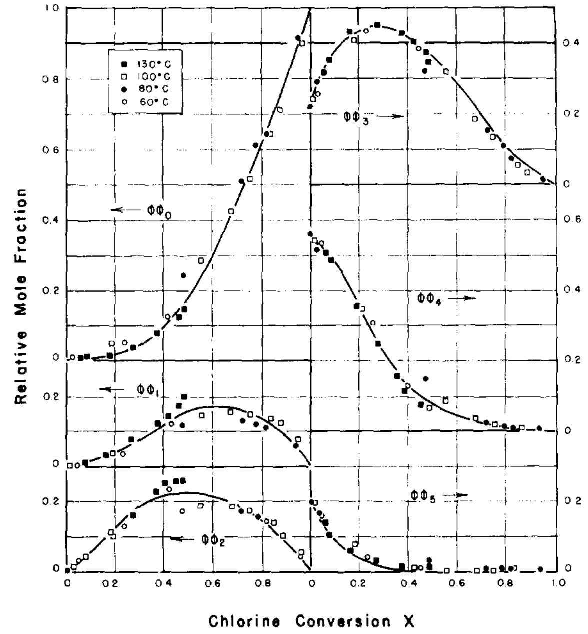


FIG. 2. Experimental data and calculated reaction paths for Aroclor 1248 hydrodechlorination over 61% Ni on kieselguhr at 50 atm of H_2 and 60–130°C.

that all activation energies are approximately equal using Ni. Figure 3 shows the effect of varying the value of a relative rate constant k'_{43}/k'_{54} from 0.35 to 0.55 on the computed reaction paths. The fit for $k'_{43}/k'_{54} = 0.40$ is sufficiently unique that the absolute error in any of the relative rate constants is probably less than ± 0.05.

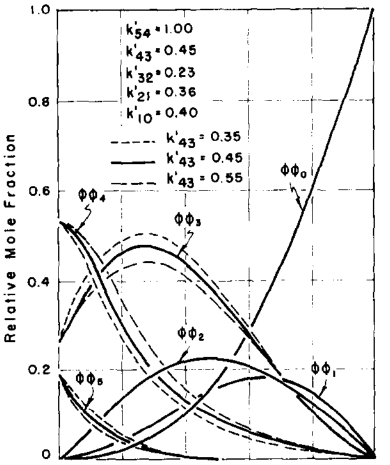


FIG. 3. Calculated reaction paths showing the sensitivity of selectivities to k'_{43}.

Figure 4 shows that at 60, 80, and 100°C the reaction exhibits an induction period which we have found to be characteristic of *in situ* additional reduction of the as-received prereduced, stabilized G 49-A Ni catalyst (*2*). After this induction period the curve is concave in nature. Note that the catalyst appeared to start to deactivate at 130°C and that there is no measurable induction period at 130°C.

In the course of these studies it was observed that within each group of PCB isomers containing the same number of chlorine atoms per molecule, certain isomers were selectively produced and reacted.

For example consider the three 1-chloro isomers. Figure 5 shows chromatograms of the monochloro isomers vs chlorine conversion at 80°C and 50 atm of H_2 pressure using Ni. The relative amount of the *ortho*-substituted isomer to the *meta–para* isomers increases with chlorine conversion. The ratio of the partially separated

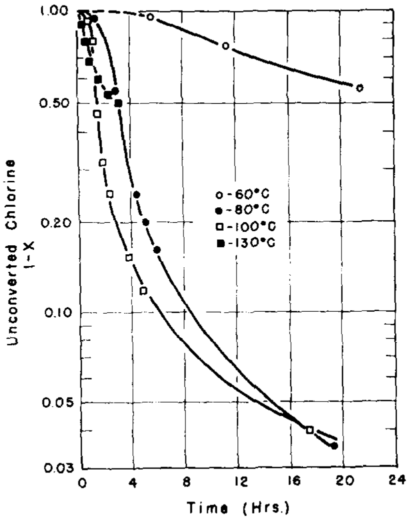


FIG. 4. Experimentally observed Aroclor hydrodechlorination kinetic behavior at 50 atm of H_2 using 61% Ni on kieselguhr catalyst.

meta and para isomers is approximately constant. Figures 6 and 7 are plots vs chlorine conversion of the relative fraction of 2- and 2,2′-isomers to total *ortho* + *meta* + *para* isomers for $\phi\phi_1$ and $\phi\phi_2$, respectively. In both cases the relative amount of *ortho*-substituted material increases with chlorine conversion, indicating that ortho-substituted chlorine is less labile than *meta*- and *para*-substituted chlorine, which are similar in reactivity.

To quantitate this behavior, we assume that any PCB mixture can be characterized by the degree of *ortho*- vs combined *meta*- + *para*-substitution alone. First-order rate expressions for the (*ortho*)O and (*meta* + *para*)MP reactions are as follows:

$$\frac{dO}{d\theta} = k_o O$$

$$\frac{dMP}{d\theta} = k_{mp} MP$$

Dividing these expressions we obtain:

$$\frac{dO}{dMP} = \frac{k_o O}{k_{mp} MP}$$

Integrating gives:

$$\frac{\log \dfrac{O}{O^0}}{\log \dfrac{MP}{MP^0}} = \frac{k_o}{k_{mp}}$$

Figure 8 is a log–log plot of O/O^0 vs MP/MP^0 that gives straight lines with slope k_o/k_{mp}. Figure 8 shows that for the 60, 80, and 100°C experiments, the value of $k_o/k_{mp} = 0.52$ while for the 130° experiment where catalyst deactivation occurred,

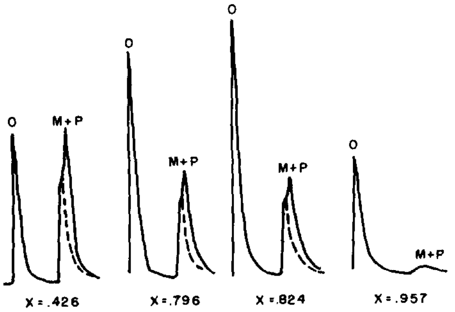


FIG. 5. Distribution of 1-chloro PCB *ortho* and *meta–para* isomers is a function of chlorine conversion at 50 atm of H_2, 80°C.

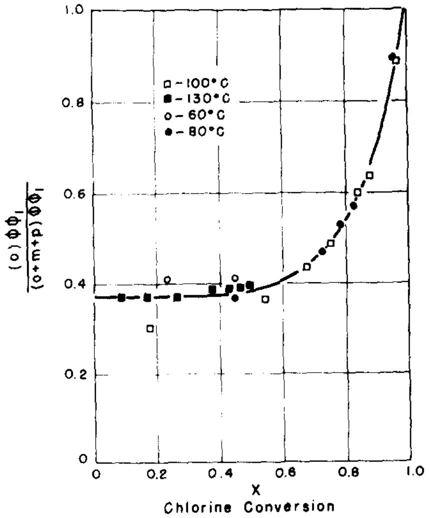


FIG. 6. The fraction of *ortho* to total (*ortho* + *meta* + *para*) isomers in monochlorobiphenyl ex Aroclor 1248 increases with conversion.

$k_o/k_{mp} = 0.31$. These values apply to the total *o*-, *m*-, and *p*-content of the Aroclor 1248.

Figure 9 is a plot of Pd on α-Al_2O_3-catalyzed vapor-phase selectivity data obtained in the pulse microreactor. The curves are calculated based on a consecutive back-mixed model; and the equation set was modified accordingly. The values of the relative rate constants were:

$\frac{k'_{43}}{k'_{54}}$	$\frac{k'_{32}}{k'_{54}}$	$\frac{k'_{21}}{k'_{54}}$	$\frac{k'_{10}}{k'_{54}}$
0.85	0.50	0.70	0.95

Ortho-substituted chlorine was also observed to be less reactive than *meta–para* in the pulse experiments over Pd on α-Al_2O_3.

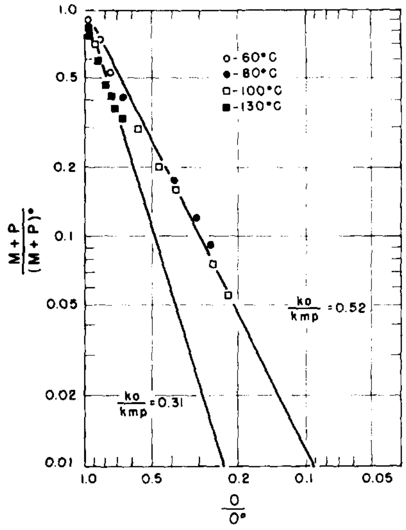


FIG. 8. The first-order rate constant ratio for total *ortho* to total $(m + p)$ isomers is $k_o/k_{mp} = 0.52$ from 60 to 100°C.

DISCUSSION AND CONCLUSIONS

Selectivity analysis has shown that aromatic hydrodechlorination of PCBs is a consecutive reaction process in which one chlorine atom at a time is removed from the biphenyl structure. Concerted reactions in which more than one chlorine is removed without intermediate desorption from the catalyst do not appear to occur. In liquid-phase DDE studies (*2*) concerted removal of aromatic and olefinic chlorine was observed. The fact that the selectivities (of species lumped by number of chlorine atoms per mole $\phi\phi_i$) are described by pseudohomogeneous first-order expressions

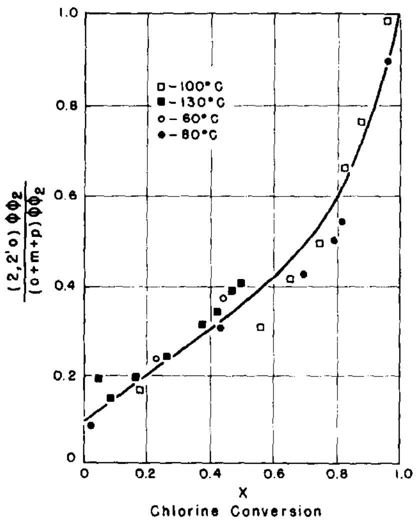


FIG. 7. The fraction of 2,2′-*ortho* to total (*ortho* + *meta* + *para*) isomers in dichlorobiphenyl ex Aroclor 1248 increases with conversion.

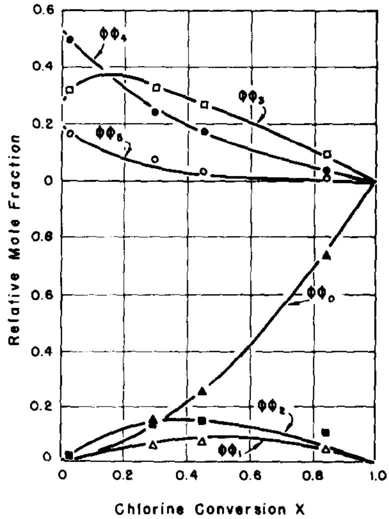


FIG. 9. Experimental data and calculated reaction paths for vapor-phase Aroclor 1248 hydrodechlorination over Pd on α-Al_2O_3 at 2.3 atm of H_2 and 220 ± 5°C (pulse microreactor).

indicates that the absolute kinetics are of the Langmuir–Hinshelwood type. The lack of temperature dependence of relative rate constants suggests the same activation energy for removal of a chlorine atom from any of the $\phi\phi_i$.

In describing the kinetics of lumped species, Luss (*10*) stresses the importance of avoiding aggregation of species with widely different kinetic behavior. In our studies where the constants for *ortho* compounds differed from *meta–para* by a factor of about 2, the behavior of a lumped species $\phi\phi_i$ could still be described by a single first-order relative rate constant over the complete conversion range (Fig. 2) indicating that lumping in this manner did not introduce serious error in the values of the k'_{ij} values obtained in these studies. The fact that the values of k'_{ij} pass through through a minimum for the Ni on Al_2O_3-catalyzed liquid phase reaction,

$$\phi\phi_5 \xrightarrow{1.0} \phi\phi_4 \xrightarrow{0.40} \phi\phi_3 \xrightarrow{0.23} \phi\phi_2 \xrightarrow{0.36} \phi\phi_1 \xrightarrow{0.40} \phi\phi_0,$$

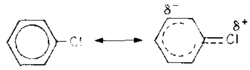
is not, however, expected.

Similar behavior was observed in the Pd–Al_2O_3-catalyzed gas-phase hydrodechlorination of PCBs where the corresponding values were

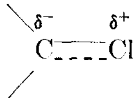
$$\phi\phi_5 \xrightarrow{1.0} \phi\phi_4 \xrightarrow{0.85} \phi\phi_3 \xrightarrow{0.50} \phi\phi_2 \xrightarrow{0.70} \phi\phi_1 \xrightarrow{0.95} \phi\phi_0.$$

Based on statistical considerations alone, one would expect the values of the relative rate constants to decrease monotonically as the number of chlorine atoms per molecule decreases. Each k'_{ij} is the product $k_{ij}K_i$, and we believe the more highly chlorinated species are more strongly adsorbed. This could in principle cause the values of k'_{ij} to decrease with chlorine number even more rapidly than the statistical probabilities.

In the case of DDE (*1*, *2*), the hydrodechlorination reaction behavior of the aromatic moiety was justified on the basis that adsorption of the benzene ring is necessary for charge delocalization:



A carbon–chlorine double bond forms, and this is actually the reactive species:



This has also been involved in explanations of earlier work on hydrodechlorination of dichloroethylenes (*6*).

Hutzinger (*5*) states that "there is considerable steric hindrance to rotation with ortho substituted biphenyl moieties and in addition this steric effect also prevents coplanarity between the two phenyl rings." Such a configuration preferentially limits the access of *ortho*-substituted chlorine to a planar surface and thereby explains the reduced activity of *ortho*-substituted chlorine which we have experimentally observed. However, as hydrodechlorination proceeds, the number of *ortho*-substituted chlorines per molecule also decreases, even though the proportion increases. This allows for a more planar configuration to exist and then be adsorbed. We believe this reduction of steric interference accounts for the increased reactivity of the more highly dechlorinated biphenyls.

ACKNOWLEDGMENTS

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