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Mechanism of Pentachloroethane Dehydrochlorination to Tetrachloroethylene

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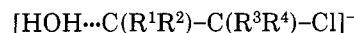
■ The dehydrochlorination of pentachloroethane to tetrachloroethylene was investigated to gain insight into mechanisms of hexachloroethane reduction as well as structure-reactivity relationships for polyhalogenated alkanes. Although the absence of deuterium exchange excludes the possibility of an $(E_{1CB})_R$ mechanism, several factors suggest the transition state possesses considerable carbanion character: the reaction is insensitive to buffer catalysis, exhibits a moderately large solvent kinetic isotope effect, and only displays a neutral mechanism at low pH. Though our results cannot rule out a stepwise $(E_{1CB})_I$ or $(E_{1CB})_{ip}$ sequence, we believe $CHCl_2CCl_3$ reacts via a concerted mechanism based on a comparison of its dehydrohalogenation kinetics with proton-exchange rates for $CHCl_3$ and $CHCl_2CF_3$. Pentachloroethane reported in the reduction of hexachloroethane to tetrachloroethylene is unlikely to result from carbanion protonation. Rather, it may be diagnostic of free-radical reduction mechanisms. Because pentachloroethane reacts relatively rapidly, future studies of hexachloroethane reduction should consider whether pentachloroethane represents a reaction intermediate instead of dismissing it as a minor side product.

Introduction

Reductive dehalogenation and dehydrohalogenation reactions dominate the transformation of many polyhalogenated alkanes in aqueous systems. Of the two classes, reductive dehalogenation is the less well studied, and its mechanisms in complex environmental samples are poorly understood. Recent studies have attempted to amend this by investigating biologically mediated and abiotic reductive transformations; several have emphasized the reduction of hexachloroethane to tetrachloroethylene (1-5), although little progress has been made in elucidating the actual reaction pathway(s). Investigations of hexachloroethane reduction by Fe(II) porphyrins (6), rat liver microsomal preparations (7), or microorganisms in groundwater samples (8) have noted pentachloroethane as a minor product. This could conceivably be generated either via hydrogen atom abstraction by a pentachloroethyl radical (formed by a one-electron reduction of hexachloroethane) or via protonation of a pentachloroethyl carbanion (resulting from a net two-electron reduction), as shown in Figure 1. Pentachloroethane can itself react to tetrachloroethylene, albeit via dehydrochlorination; several possible mechanisms could involve a pentachloro-

ethyl carbanion intermediate. Understanding the details through which this elimination reaction proceeds should provide some basis for weighing the relative likelihood of the potential hexachloroethane reduction pathways. In addition, knowing the rate at which pentachloroethane reacts should prove useful in assessing whether it represents a side product or a reaction intermediate. Finally, comparing the kinetics of pentachloroethane elimination to rates for other polychlorinated ethanes should provide substantial insight into the influence of structural factors on reactivity in this class of important environmental contaminants.

Dehydrohalogenation mechanisms for pentachloroethane such as the E_1 and the $(E_{1CB})_{anion}$ mechanisms can be ruled out by the observed dependence of reaction rate on pH (among other factors). Reactions exhibiting second-order kinetics can occur by two different classes of mechanism (9), referred to as E_2 and E_{1CB} (Figure 2); the latter path is frequently ignored by introductory organic chemistry textbooks. In the E_2 mechanism (Figure 2a), proton loss and halide ion elimination occur in a concerted fashion, whereas E_{1CB} reactions (Figure 2b) are characterized by the initial formation of a carbanion intermediate. Depending on the relative rates of reprotonation and elimination steps, this carbanion can either revert to starting material via a reversible proton-transfer step [$(E_{1CB})_R$ mechanism] or proceed to form the olefin with little reprotonation [$(E_{1CB})_I$ mechanism]. Closely related to the $(E_{1CB})_R$ mechanism is the $(E_{1CB})_{ip}$ mechanism, the difference being that in the latter case, the free carbanion is not formed, but remains intimately associated as an ion pair or hydrogen-bonded pair with the conjugate acid of the former base, as designated by the intermediate



in Figure 2b. These mechanisms are kinetically indistinguishable: all are characterized by a first-order dependence on the concentration of the effective base, as indicated in Figure 2.

A key question is whether pentachloroethane reacts via an $(E_{1CB})_R$ or an $(E_{1CB})_{ip}$ mechanism. If so, any pentachloroethyl carbanion formed during the reduction of hexachloroethane would be expected to undergo proton transfer to form pentachloroethane. Conversely, if pentachloroethane were to react via an E_2 or an $(E_{1CB})_I$ mechanism, this implies a pentachloroethyl carbanion is

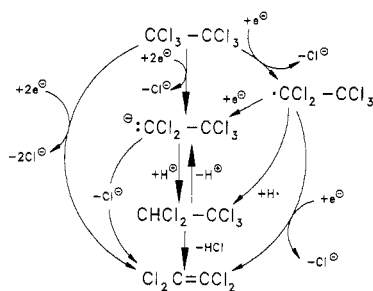


Figure 1. Potential pathways for the reduction of hexachloroethane to pentachloroethane and tetrachloroethylene, and for the dehydrochlorination of pentachloroethane to tetrachloroethylene.

so unstable under ambient conditions that either it is unlikely ever to be formed (whether from hexachloroethane or pentachloroethane) or at least it should decompose to tetrachloroethylene rather than persist long enough to become protonated. In this case, any pentachloroethane produced from hexachloroethane might be diagnostic of a free-radical reduction pathway.

Most simple alkyl halides are believed to react via concerted E_2 mechanisms, although many exceptions exist. A number of compounds have been shown to undergo proton-exchange reactions, indicative of $(E_{1CB})_R$ -like mechanisms. These include di- and trihaloethylenes (10–12), haloforms (13–18), and several pentahaloethanes (all 1,1,1-trifluoro-2,2-dihaloethanes; ref 19). These substrates are all characterized by acidic hydrogens and unfavorable leaving groups. Pentachloroethane also has an acidic hydrogen (in terms of the inductive effects of the five chlorine atoms at the α - and β -carbons), but any of the chlorines bonded to the sp^3 -hybridized C_α constitute a much better leaving group than the halogens in the above examples. Whether the latter factor is sufficient to favor the E_2 mechanism over an E_{1CB} mechanism is difficult to predict

a priori. Several chlorinated and brominated substrates with similar inductive effects at C_β may react via E_{1CB} pathways. An $(E_{1CB})_I$ mechanism has been claimed for DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) and some of its analogues (20, 21), although this has been contested by other researchers for reactions under somewhat different conditions (22). Other evidence indicates several substituted polyhaloethanes, including $C_6H_5CHClCF_2Cl$, $C_6H_5CHBrCF_2Br$, and $C_6H_5CHBrCH_2Br$, react via an $(E_{1CB})_{IP}$ mechanism even in protic solvents (23, 24). These substrates all contain phenyl substituents capable of stabilizing a carbanion, but some stabilization might also be expected from the chlorines in pentachloroethane. One researcher (25) has even gone so far as to question the prevalence of E_2 reactions, suggesting that E_{1CB} reactions may be much more common than previously recognized.

Walraevens et al. (26) studied the reaction of pentachloroethane in water at high pH via conductivity measurements. They suggested the absence of significant buffer catalysis and the negative value computed for the activation entropy might reflect an E_{1CB} mechanism, without conducting further tests to support this hypothesis. Although Walraevens et al. were not specific, in all probability they envisioned an $(E_{1CB})_R$ mechanism; other E_{1CB} mechanisms, which had only very rarely been described at the time their study was conducted, are more likely to be subject to buffer catalysis.

In the present study, we have measured parameters required to model the transformation of pentachloroethane under environmental conditions (near-ambient temperatures and low to moderate pH). Very recently, Jeffers et al. (27) and Cooper et al. (28) published results of similar kinetic experiments without, however, proposing any mechanistic interpretation. These two studies confirm our measured activation parameters, and the study of Jeffers et al. (27) provides evidence of a neutral dehydrochloro-

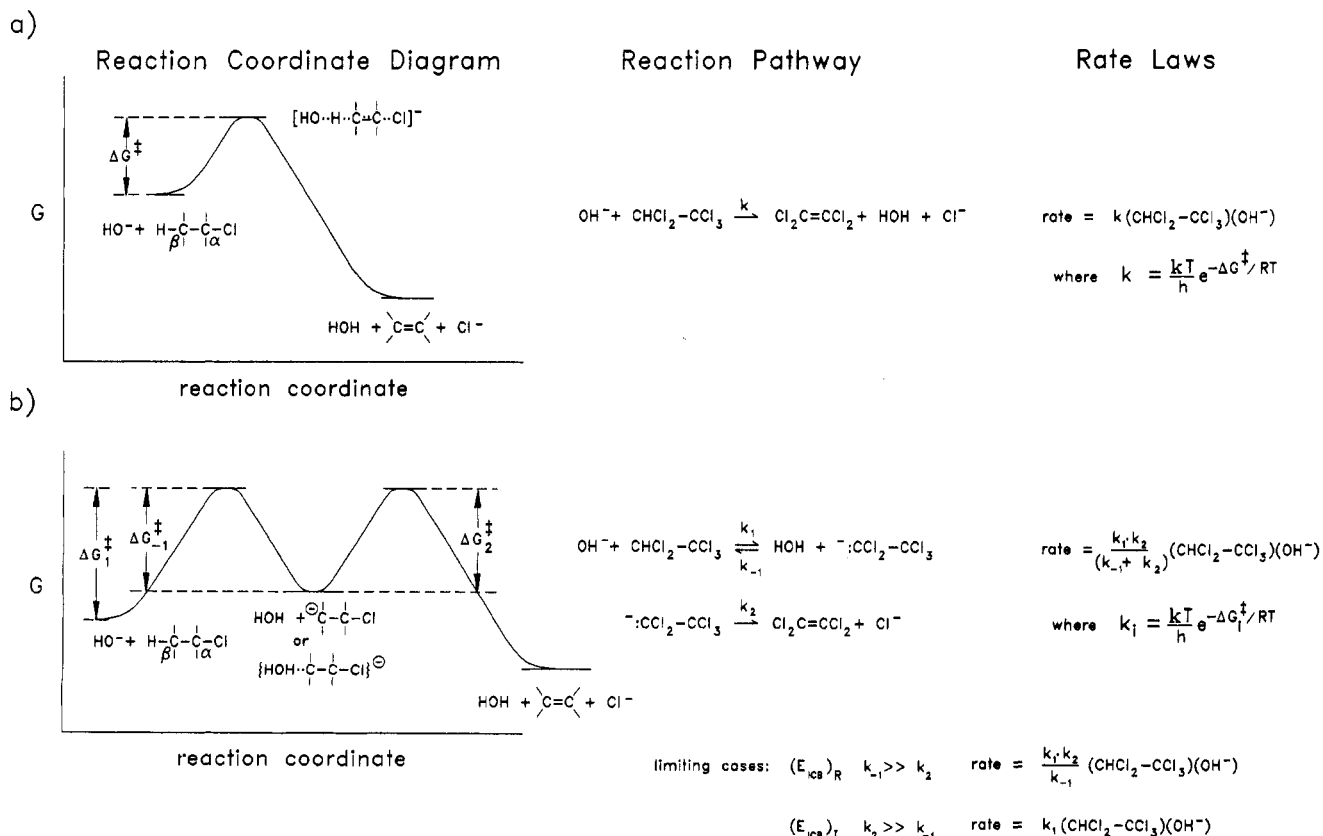


Figure 2. Potential mechanisms of HCl elimination from pentachloroethane. (a) E_2 mechanism: concerted elimination of HCl. (b) E_{1CB} mechanisms: initial formation of a carbanion intermediate.

mination reaction not observed in our experiments. The primary objective of the present study was to obtain evidence concerning the mechanism by which pentachloroethane reacts to permit us to evaluate its significance when observed during hexachloroethane reduction. This study complements our continuing investigations of polyhalogenated alkane reduction mechanisms, both by microorganisms in anoxic groundwater and by reduced sulfur species under clean chemical conditions and in sulfide-rich natural waters (8).

Materials and Methods

Reagents. Dehydrochlorination rates were measured in buffered systems containing one or more of the following reagent-grade salts: sodium benzoate, sodium acetate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium sulfide, and sodium tetraborate decahydrate. Buffer solutions were prepared with the appropriate salt or salts plus sufficient HCl to bring the pH approximately to the pK_a of the buffer acid. Although the buffers used are generally fairly dilute, concentrations are high enough relative to initial pentachloroethane levels that we expect at most a 3% change in the hydroxyl ion concentration during the course of the reaction (<0.2% for the most of the buffers used). Ionic strength was adjusted as required with NaCl. Mercuric chloride (10 mg/L) was added to inhibit microbial activity for all but the hydrogen sulfide buffer and the D_2O buffer used for the isotope-exchange experiment. For the latter experiment, D_2O (99.9%) was obtained from Cambridge Isotope Laboratory, Woburn, MA. Otherwise, aqueous solutions were prepared with high-purity (>15 M Ω /cm) deionized distilled water prepared with a Milli-Q water system (Millipore Corp., Bedford, MA).

Determinations of pH were performed at the appropriate temperature with an Orion Model SA 720 pH/ISE meter and an Orion Ross combination pH electrode. For the experiment in D_2O , the pH meter was calibrated against buffers in normal water, and the meter reading converted to pD as described by Perrin and Dempsey (29). Hydroxyl ion activities were computed from pH measurements by using pK_w values of 13.9965 at 25 °C and 13.6801 at 35 °C. The OD^- ion activity was obtained by using a pK of 14.869 at 25 °C (30). For determining second-order rate constants, OH^- or OD^- concentrations were calculated from ion activities by using activity coefficients estimated from the extended Debye-Hückel relationship for solutions with $I \leq 0.05$ and from the Davies equation for solutions with $I = 0.1$ equiv/L.

Stock solutions of $CHCl_2CCl_3$ (96%) (Aldrich) and $Cl_2C=CCl_2$ (98%) (MCB) were dissolved in methanol for spiking experimental flasks and preparing aqueous standard solutions. For most experiments, either CCl_3F (99+%) or $Cl_2C=CHCl$ was included to establish the integrity of our glass reaction vessels against losses of volatile compounds. For the isotope-exchange experiment, a stock solution of $CHCl_2CCl_3$ was prepared in CH_3OD (99.5+%) immediately prior to use. All halogenated compounds were used as received without further purification. Gas chromatography (GC) and combined gas chromatography/mass spectrometry (GC/MS) analyses of the $CHCl_2CCl_3$ indicated it contained low levels (~2%) of $Cl_2C=CCl_2$; corrections were generally not required for this contamination.

For most experiments, samples were analyzed via cold on-column direct aqueous injection electron capture detection gas chromatography (31), using external aqueous standards prepared freshly each day from methanol stock solutions. For the isotope-exchange experiment and the

buffer catalysis experiment conducted at pH 4.6, in which analyses were conducted of hexane extracts, standards were prepared by diluting alkyl halides directly into hexane.

Glassware. Most experiments were performed in three-necked round-bottom flasks (250-mL nominal volume) fitted with ground-glass stopcock adapters or stoppers. Aqueous standards were prepared by spiking stock solutions into 20- or 50-mL glass syringes filled with water. A 50-mL glass syringe was also used as a reaction vessel for the isotope-exchange experiment instead of a three-necked flask to permit removal of relatively large aliquots for solvent extraction without creating headspace.

Kinetic Experiments. After reaction vessels were filled with buffer solutions, leaving minimal headspace to prevent volatilization (generally <1-mL headspace to 300-mL total volume), they were transferred to water baths to reach thermal equilibrium (either at 24.9 ± 0.09 °C or 35.0 ± 0.18 °C). Reaction vessels were then spiked with 7–100- μ L aliquots of CCl_3F or $Cl_2C=CHCl$ plus $CHCl_2CCl_3$ in methanol (or 7.5 μ L of $CHCl_2CCl_3$ in CH_3OD) to give initial pentachloroethane concentrations of 0.5–50 μ M. The resulting methanol concentration (less than 1.5×10^{-4} mol fraction) is too small to influence reaction rates. After an initial mixing period and sampling, reaction vessels were returned to the water baths for incubation in the dark.

Aliquots were periodically removed for analysis. In most cases, only a few microliters of solution were removed for injection directly onto the GC column. For some experiments, however, a preliminary dilution step was required. To quench reactions that proceeded rapidly at high pH (>8), 100- μ L samples were diluted into 2-mL samples of dilute HCl to lower the pH below pH 6. Samples were then stored on ice for a few hours until analyses could be completed. Experiments conducted at pH 8 with and without a dilution step showed no significant differences. For the experiment conducted with the H_2S buffer, 100- μ L sample aliquots were diluted into 2 mL of deoxygenated deionized water prior to direct aqueous injection analysis. This enabled us to avoid the electron capture detector quenching we have observed at high $(H_2S)_T$ concentrations. For the buffer catalysis experiments conducted at pH 4.6, which required relatively concentrated buffers, direct aqueous injection GC was not used to avoid baseline problems we have encountered with such solutions. Rather, 100- μ L aliquots were periodically removed from the reaction vessels and extracted with 1 mL of hexane. One-milliliter samples were also extracted with 0.5 mL of hexane (containing 1,1,1,2-tetrachloroethane as an internal standard) for GC/MS analysis in the isotope-exchange experiment.

For most experiments, efforts were made to monitor the reaction over at least 2–3 half-lives to ensure tetrachloroethylene was in fact the sole product. At pH <5, however, where half-lives were very long (>100–1900 days), incubations were only monitored for 9 or 10 weeks.

Data Analysis. For each experiment, monitoring $CHCl_2CCl_3$ disappearance and $Cl_2C=CCl_2$ appearance permitted independent estimates of pseudo-first-order rate constants. These were generally obtained by fitting the $CHCl_2CCl_3$ data via a regression of the form $\ln(CHCl_2CCl_3) = \ln(CHCl_2CCl_3)_0 - k_{obs}t$ or via a nonlinear fit of the $Cl_2C=CCl_2$ data to an equation of the form $(Cl_2C=CCl_2) = (CHCl_2CCl_3)_0[1 - \exp(-k_{obs}t)]$. At low pH (<5), $Cl_2C=CCl_2$ data were fit to $(Cl_2C=CCl_2) = (CHCl_2CCl_3)_0[1 - \exp(-k_{obs}t)] + (Cl_2C=CCl_2)_0$ to incorporate the small amount of $Cl_2C=CCl_2$ present as a contaminant in the $CHCl_2CCl_3$. For the $Cl_2C=CCl_2$ regressions at low pH, the

Table I. Results of Dehydrochlorination Experiments Conducted at Low Ionic Strength (0.005 equiv/L) in H₂O

pH	mM buffer	N ^a	from CHCl ₂ CCl ₃		from Cl ₂ C=CCl ₂		predicted <i>k</i> , ^b s ⁻¹
			<i>k</i> _{obs} , s ⁻¹	<i>R</i> ²	<i>k</i> _{obs} , s ⁻¹	<i>R</i> ²	
25 °C Results							
4.15	2.5 (benzoate) _T	10	1.41 × 10 ⁻⁸	0.5386	4.19 × 10 ⁻⁹	0.9612	4.20 × 10 ⁻⁹
4.71	2.5 (acetate) _T	10	3.35 × 10 ⁻⁸	0.8849	1.14 × 10 ⁻⁸	0.9865	1.53 × 10 ⁻⁸
7.09	2.5 (PO ₄) _T	10	3.28 × 10 ⁻⁶	0.9996	3.59 × 10 ⁻⁶	0.9806	3.66 × 10 ⁻⁶
7.94	1.25 (PO ₄) _T + 1.25 (BO ₃) _T	11	2.90 × 10 ⁻⁵	0.9845	3.75 × 10 ⁻⁵	0.9772	2.59 × 10 ⁻⁵
7.98	1.67 (PO ₄) _T + 1.67 (BO ₃) _T	11	3.02 × 10 ⁻⁵	0.9975	4.07 × 10 ⁻⁵	0.9923	2.84 × 10 ⁻⁵
9.10	2.5 (BO ₃) _T	17	4.39 × 10 ⁻⁴	0.9991	4.60 × 10 ⁻⁴	0.9982	3.75 × 10 ⁻⁴
35 °C Results							
4.14	2.5 (benzoate) _T	10	3.70 × 10 ⁻⁸	0.9016	2.20 × 10 ⁻⁸	0.9865	2.48 × 10 ⁻⁸
4.68	2.5 (acetate) _T	10	9.83 × 10 ⁻⁸	0.9666	7.74 × 10 ⁻⁸	0.9906	8.62 × 10 ⁻⁸
7.06	2.5 (PO ₄) _T	7	2.03 × 10 ⁻⁵	0.9937	2.53 × 10 ⁻⁵	0.9939	2.07 × 10 ⁻⁵
7.90	1.25 (PO ₄) _T + 1.25 (BO ₃) _T	15	1.44 × 10 ⁻⁴	0.9988	1.53 × 10 ⁻⁴	0.9949	1.43 × 10 ⁻⁴

^aN, number of samples. ^bSee text.

(CHCl₂CCl₃)₀ value used was constrained to equal the value determined from the regression to the CHCl₂CCl₃ data. In all other cases, parameters were independently obtained to avoid assumptions concerning product distribution.

Gas Chromatography. GC analyses were performed with a Carlo-Erba Fractovap Series 2150 or a Carlo-Erba HRGC 5160 unit equipped with a cold on-column injector, a 30 m × 0.32 mm i.d. thick film (5-μm cross-linked SE-30 equivalent) fused-silica capillary column (Restek Corp., Bellefonte, PA), and a ⁶³Ni electron capture detector. Concentrations were determined by comparing peak areas for samples to those measured for external standards. Because the detector response was nonlinear, standards were analyzed each day generally at five or more concentrations spanning the ranges measured in the samples, and a calibration curve was obtained by fitting the responses to a curve of the form (area) = *a*(picomoles)^{*b*}.

GC/MS Analyses. GC/MS measurements of hexane extracts were conducted with a Hewlett-Packard Model 5995 gas chromatograph/mass spectrometer. The column used was a 30-m, thin-film (0.25 μm) fused-silica capillary column with a nonpolar DB-5 (cross-linked SE-54 equivalent) phase (J&W Scientific, Folsom, CA). The mass spectra were recorded under electron impact ionization at 70 eV. For most analyses, only the following ions were monitored to maximize sensitivity: *m/e* 116–119, 133, and 164–172. Complete scans (*m/e* 59–210) were, however, performed on selected samples to confirm the identity of the transformation product.

Results

Reaction Rate vs pH. Example results of our experiments conducted with dilute buffers are shown in Figure 3. Pentachloroethane transformation under the conditions studied is relatively rapid, in many cases occurring over a period of hours to weeks. As shown in Figure 3a, concentrations of the CCl₃F tracer used to validate our reaction vessel subsampling technique displayed no tendency to decrease even over as long a period of 63 days. This compound is much more volatile (*H* = 3.65 mol L⁻¹(air)/mol L⁻¹(water); ref 32) than either Cl₂C=CCl₂ (*H* ≈ 0.5–0.7; refs 33 and 34) or CHCl₂CCl₃ (*H* ≈ 0.09; ref 33). The disappearance of CHCl₂CCl₃ can thus be attributed solely to chemical transformation, rather than volatilization. Rate constants obtained at low buffer concentrations are summarized in Table I, along with information concerning buffer compositions. As demonstrated by the data in this table, transformation rates are strongly dependent on pH.

At pH < 5, *k*_{obs} values obtained from the pentachloroethane data appear somewhat larger than those obtained from the tetrachloroethylene data. One explanation for

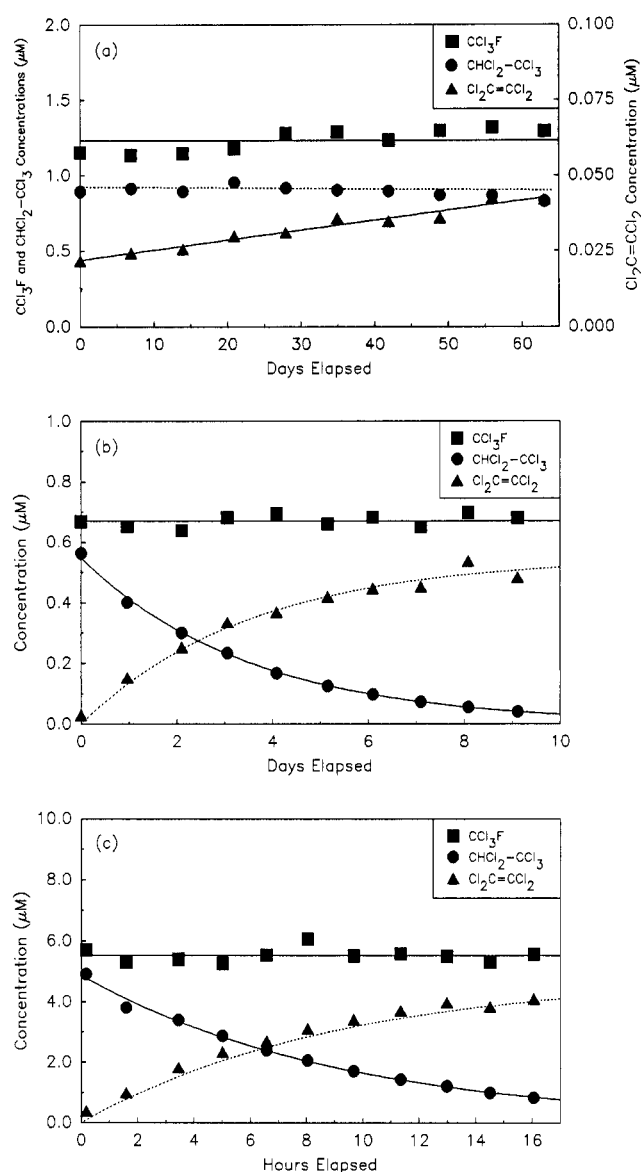


Figure 3. Example time courses showing transformation of pentachloroethane to tetrachloroethylene at 25 °C at (a) pH 4.15, (b) pH 7.09, and (c) pH 7.98. Note variations in scales. Symbols represent measured concentrations. Solid lines represent model fits or (in the case of CCl₃F data) mean concentration. Dashed lines represent predicted values.

this apparent discrepancy might simply lie in difficulties associated with making precise estimates of reaction rates from parent compound disappearance at relatively early times. Because pentachloroethane reacts very slowly at

low pH and 25–35 °C, it is difficult to obtain a very accurate estimate of its reaction rate from the pentachloroethane data, which display relatively small changes. For these experiments, the tetrachloroethylene data (which exhibit much larger changes) provide a more precise estimate. Despite the apparent discrepancy in observed rates at low pH, rate constants obtained from model fits to the tetrachloroethylene data still predict pentachloroethane concentrations quite well, as indicated on Figure 3a.

An alternative explanation for the apparent discrepancy in k_{obs} values might be that at low pH, pentachloroethane is reacting via some mechanism in addition to dehydrochlorination, such as perhaps a nucleophilic substitution reaction. In such a case, the integrated rate expression for pentachloroethane can be written as

$$(\text{CHCl}_2\text{CCl}_3) = (\text{CHCl}_2\text{CCl}_3)_0 \exp[-(k_E + k_N)t] \quad (1)$$

where k_E refers to the pseudo-first-order rate constant for dehydrochlorination to tetrachloroethylene and k_N to the corresponding rate constant for the hypothetical substitution reaction. In this case, the observed rate constant k_{obs} would correspond to the sum of $k_E + k_N$. Similarly, the expression for tetrachloroethylene would be given as

$$(\text{Cl}_2\text{C}=\text{CCl}_2) = (\text{CHCl}_2\text{CCl}_3)_0 [k_E / (k_E + k_N)] [1 - \exp[-(k_E + k_N)t]] \quad (2)$$

At relatively small time, however, $\exp[-(k_E + k_N)t]$ approaches $1 - (k_E + k_N)t$, and the expression simplifies to

$$(\text{Cl}_2\text{C}=\text{CCl}_2) \approx (\text{CHCl}_2\text{CCl}_3)_0 k_E t \quad (3)$$

i.e., the observed rate constant k_{obs} corresponds to k_E when product accumulation is monitored at early time. Although the results of Jeffers et al. (27) indicated quantitative conversion to tetrachloroethylene under all conditions investigated, their experiments at low pH were conducted at substantially higher temperatures than our experiments; elimination reactions, which frequently exhibit larger activation energies than other potential mechanisms such as substitution reactions, could contribute to a greater extent at higher temperatures than at lower temperatures. A polar product might well have been missed by our analytical technique.

For the experiments conducted at $\text{pH} \geq 7$, there is rarely any significant difference (at the 95% confidence level) between k_{obs} [or $(\text{CHCl}_2\text{CCl}_3)_0$] values obtained from the pentachloroethane data vs those obtained from the tetrachloroethylene data. For these experiments, the pentachloroethane data generally provide more precise estimates of rate constants than the tetrachloroethylene data, as indicated by the R^2 values in Table I. Rate constants obtained from model fits to the pentachloroethane data successfully predict tetrachloroethylene concentrations, as shown in Figure 3b and c. The close correspondence at higher pH between predicted and observed concentrations indicates that tetrachloroethylene represents the predominant if not the sole product of pentachloroethane transformation.

Figure 4 summarizes the relationship between rates shown in Table I and the pH at which the measurements were made. A regression on $\log k_{\text{obs}}$ vs $\log (\text{OH}^-)$ at 25 °C yielded a model fit of the form $\log k_{\text{obs}} = 1.05 (\pm 0.02) \log (\text{OH}^-) + 1.76 (\pm 0.06)$, with $R^2 = 0.9996$ (values in parentheses reflect 95% confidence intervals); similarly, at 35 °C the fit is of the form $\log k_{\text{obs}} = 1.01 (\pm 0.02) \log (\text{OH}^-) + 1.97 (\pm 0.06)$, with $R^2 = 0.9997$. In performing the regressions, the values of k_{obs} were weighted according to their estimated standard error as described by Bevington (ref 35, p 182). Because regressions performed independently on k_{obs} values obtained from the pentachloro-

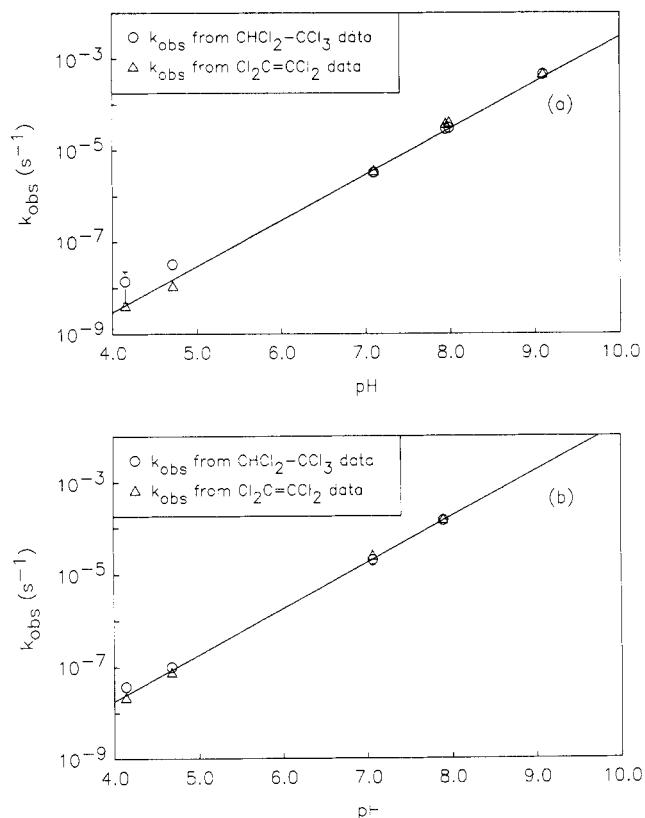


Figure 4. Observed rate constants for low ionic strength experiments as a function of pH. Solid lines indicate rates predicted from calculated second-order rate constants; (a) 25 °C results; (b) 35 °C results.

ethane data and those obtained from the tetrachloroethylene data gave results that were not significantly different at the 95% confidence level, rate constants at each temperature were pooled to yield an improved estimate.

The slopes of the model fits are very close to 1, indicating the reaction of pentachloroethane is first order in OH^- at both temperatures throughout the pH range investigated; our results do not provide any evidence for a neutral mechanism involving H_2O as a base. Analysis of our data assuming the reaction is truly first order in OH^- (again weighting k_{obs} values according to their estimated standard error) provides estimates for the second-order rate constant k_{OH^-} of $27.3 (\pm 0.3) \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $79.7 (\pm 1.6) \text{ M}^{-1} \text{ s}^{-1}$ at 35 °C. Pseudo-first-order rate constants predicted from this k_{OH^-} value are shown in Figure 4 and also in Table I. Omitting the k_{obs} values determined at pH 4.1–4.2 does not significantly affect the magnitudes of k_{OH^-} estimates at either temperature. Our results correspond to a half-life for pentachloroethane of approximately 2.9 days at pH 7, 25 °C. This is somewhat less than the half-life of 3.5 days calculated from the results of Walraevens et al. (26) or the value of 3.7 days given by Jeffers et al. (27) and greater than the value of 1.7 days given by Cooper et al. (28), yet still within the 95% confidence limits reported by each of these investigators or computed from their data.

Isotope-Exchange Experiment. To investigate the possibility of an $(\text{E}_{\text{ICB}})_\text{R}$ mechanism, we conducted an isotope-exchange experiment in D_2O . The buffer used in this experiment contained 10 mM $(\text{PO}_4)_\text{T}$ plus 10 mM $(\text{BO}_3)_\text{T}$, with an ionic strength of approximately 0.025 equiv/L and pD 8.69. This buffer was spiked to give an initial pentachloroethane- h concentration of 50 μM . Under the chromatographic conditions used in GC/MS analyses of hexane extracts of this buffer, tetrachloroethylene,

Table II. Results of Dehydrochlorination Experiments Conducted at 25 °C in H₂O To Investigate General-Base (Buffer) Catalysis^a

pH	mM buffer	N ^b	from CHCl ₂ CCl ₃		from Cl ₂ C=CCl ₂		predicted <i>k</i> , ^c s ⁻¹
			<i>k</i> _{obs} , s ⁻¹	<i>R</i> ²	<i>k</i> _{obs} , s ⁻¹	<i>R</i> ²	
6.95	15.3 (H ₂ S) _T + 0.5 (PO ₄) _T	11	2.79 × 10 ⁻⁶	0.9989	3.75 × 10 ⁻⁶	0.9930	3.04 × 10 ⁻⁶
4.61	5 (acetate) _T	11	5.32 × 10 ⁻⁸	0.8443	7.60 × 10 ⁻⁹	0.9715	1.45 × 10 ⁻⁸
4.62	25 (acetate) _T	11	1.30 × 10 ⁻⁸	0.1226	1.07 × 10 ⁻⁸	0.9811	1.48 × 10 ⁻⁸
4.62	50 (acetate) _T	11	2.67 × 10 ⁻⁸	0.5068	9.71 × 10 ⁻⁹	0.9810	1.50 × 10 ⁻⁸
4.63	75 (acetate) _T	11	3.25 × 10 ⁻⁸	0.7373	8.40 × 10 ⁻⁹	0.9742	1.51 × 10 ⁻⁸
4.63	100 (acetate) _T	11	3.44 × 10 ⁻⁸	0.8276	8.86 × 10 ⁻⁹	0.9728	1.53 × 10 ⁻⁸

^a Ionic strength 0.05 equiv/L for H₂S/HS⁻ buffer and 0.1 equiv/L for acetic acid/acetate buffers. ^b *N*, number of samples. ^c Predicted pseudo-first-order rate in absence of buffer catalysis.

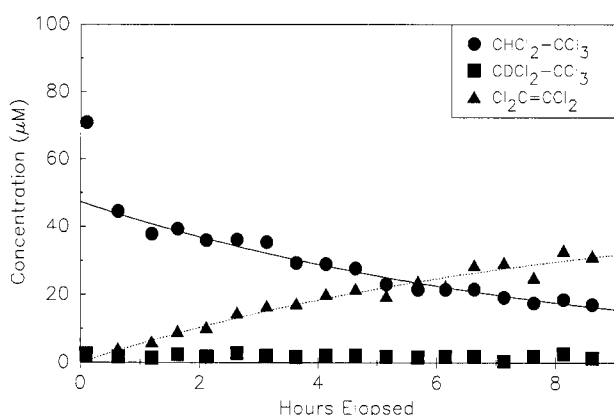


Figure 5. Results of isotope-exchange experiment conducted in D₂O at 25 °C. Solid line through CHCl₂CCl₃ data represents exponential fit; dashed line through Cl₂C=CCl₂ data shows predicted values assuming all CHCl₂CCl₃ is converted to Cl₂C=CCl₂.

1,1,1,2-tetrachloroethane, and pentachloroethane were all fully resolved. Lacking a deuterated pentachloroethane standard, however, we could not be certain that this would also be the case for pentachloroethane-*d* and pentachloroethane-*h*; our method of data analysis assumed the labeled and unlabeled pentachloroethane would coelute. In analyzing each sample, the ion *m/e* 166 (corresponding to ³⁵Cl₃³⁷Cl¹²C₂) was used to calculate tetrachloroethylene concentrations. The ion *m/e* 117 (³⁵Cl₃¹²C) was used to monitor total pentachloroethane. Because pentachloroethane lacks a parent ion, pentachloroethane-*h* concentrations were computed from *m/e* 165 (³⁵Cl₄¹²C₂H) [after correcting for ³⁵Cl₄¹³C¹²C based on ¹³C abundances reported by McLafferty (36)]. The ion *m/e* 168 (³⁵Cl₃³⁷Cl¹²C₂D) proved useful for calculating pentachloroethane-*d* concentrations (after similar corrections for ³⁵Cl₃³⁷Cl¹³C¹²CH and ³⁵Cl₂³⁷Cl₂¹²C₂).

The results are shown in Figure 5. After an initial mixing period, pentachloroethane concentrations exhibited first-order decay; pentachloroethane-*h* concentrations computed from *m/e* 165 were essentially equal to total pentachloroethane calculated from *m/e* 117. No trend was detected in the results for pentachloroethane-*d*, which remained at our detection limit. Pentachloroethane-*h* disappearance was accompanied by the production of tetrachloroethylene. The pseudo-first-order rate constant calculated from pentachloroethane disappearance ($3.4 \times 10^{-5} \text{ s}^{-1}$) is not significantly different from the rate constant calculated from tetrachloroethylene appearance ($3.6 \times 10^{-5} \text{ s}^{-1}$). As in previous graphs, the dashed line through the tetrachloroethylene data represents a prediction based on the fit to the pentachloroethane-*h* data, assuming tetrachloroethylene is the sole product of pentachloroethane transformation. The second-order rate constant *k*_{OD⁻} that can be estimated from the pentachloroethane data ($44.2 \text{ M}^{-1} \text{ s}^{-1}$) is 1.6 times that determined for *k*_{OH⁻} at 25 °C,

within the range of solvent isotope effects measured for E₂ reactions (37, 38) and slightly larger than reported *k*_{OD⁻}/*k*_{OH⁻} ratios of ~1.5 for (E₁CB)₁ reactions (39). Substantially larger solvent isotope effects as great as 7.7 have been reported for (E₁CB)_R reactions (40).

Buffer Catalysis. Two buffer systems were used to investigate general-base (buffer) catalysis at 25 °C, H₂S/HS⁻ and acetic acid/acetate. Buffer compositions used and experimental results are summarized in Table II, along with rates predicted (in the absence of buffer catalysis) from *k*_{OH⁻} and the measured pH.

Initial experiments (using H₂S/HS⁻ as a buffer) failed to display any buffer catalysis, in agreement with the observations of Walraevens et al. (26) with phenolate buffers. The second-order rate constant computed by using the measured OH⁻ concentration ($25 \text{ M}^{-1} \text{ s}^{-1}$) is 8% less than our estimate of *k*_{OH⁻} from the studies conducted in the absence of bisulfide ion. This discrepancy is within our estimates of experimental error at this pH, based on duplicate measurements at pH 8, 25 °C (Table I), as well as on the results of preliminary replicate experiments that were carried out at pH 4–7 (data not included).

Experiments conducted with varying concentrations of total acetate at pH 4.6 also failed to reveal buffer catalysis. As with other experiments at this pH, the extent of pentachloroethane transformation during the course of these incubations was so slight that the tetrachloroethylene data are considered to provide a better estimate of the dehydrochlorination rate. Subtracting the contribution of *k*_{OH⁻}(OH⁻) from the observed rates should yield the acetate-promoted rate; no significant trend was discernable in a regression of these rates vs acetate concentration (*R*² = 0.07). This indicates differences in observed rates are dominated by experimental error rather than by buffer catalysis. Neglecting any potential contribution from an acetate-promoted reaction, the *k*_{OH⁻} values calculated in these experiments exhibited a relative standard deviation of 13%, an estimate of experimental error that can be used in establishing a lower limit on the Brønsted coefficient β.

Discussion

Mechanism of Pentachloroethane Dehydrochlorination. Available Tests of Mechanism. Several tests have been proposed (9, 41, 42) for differentiating between E₂ and E₁CB reactions: those pertinent are summarized in Table III. For purposes of the present study, the isotope-exchange experiment provides the most definitive test. The lack of any detectable conversion of pentachloroethane-*h* to pentachloroethane-*d* through observations over more than 1 half-life proves that proton transfer is not faster than chloride ion elimination, decisively ruling out an (E₁CB)_R mechanism.

Many of the remaining tests in Table III can also be used to distinguish between the various possibilities, yet une-

Table III. Tests Useful in Differentiating between E_2 and E_{1CB} Mechanisms of Base-Promoted Dehydrohalogenation Reactions^a

$$B^- + H(D)-\underset{\beta}{\overset{|}{C}}-\underset{\alpha}{\overset{|}{C}}-X \longrightarrow BH(D) + \overset{|}{C}=\overset{|}{C} + X^-$$

test	mechanism			
	E_2^b	$(E_{1CB})_I$	$(E_{1CB})_{ip}$	$(E_{1CB})_R$
β -protium exchange faster than elimination?	no	no	no ^c	yes
ΔV^\ddagger value ^d	negative	positive ^e	positive	positive
k_H/k_D	2-8	2-8	1-1.2 ^f	1.0 ^g
leaving group element or isotope effect	small	small to negligible	substantial	substantial
ΔS^\ddagger value ^h		more negative for E_2 or $(E_{1CB})_I$ than for $(E_{1CB})_R$		
susceptible to buffer catalysis?	yes	yes	yes ⁱ	no

^a Primarily adapted from ref 42. ^b Assuming an E_2 transition state with considerable carbanion character. ^c An example of an $(E_{1CB})_{ip}$ reaction accompanied by protium exchange has, however, been described by Koch et al. (24). ^d Results predicted by Brower et al. (41). ^e Note, however, that Brower et al. (41) measured a negative value for 2-chloroethyl phenyl sulfone, a substrate that appears to react via an $(E_{1CB})_I$ mechanism. ^f Substantially larger values have been reported for some substrates which nonetheless appear to react via an $(E_{1CB})_{ip}$ mechanism [e.g., $k_H/k_D = 4.34$ for $C_6H_5CLBrCH_2Br$ (23)]. ^g Somewhat larger values have, however, been reported for $(E_{1CB})_R$ -like reactions [e.g., 1.42 for chloroform (43)]. ^h Results predicted by Saunders and Cockerill (9); by analogy, results for $(E_{1CB})_{ip}$ reactions might be assumed to resemble $(E_{1CB})_R$ results. ⁱ Only when ion pair assists in removal of leaving group or when first step is rate-limiting.

quivocally identifying the correct mechanism in the absence of β -hydrogen exchange still represents a challenging problem in physical organic chemistry. Although measuring the volume of activation ΔV^\ddagger , primary kinetic isotope effect k_H/k_D , and leaving group isotope or element effects might help pinpoint the mechanism, such experiments are difficult to conduct, requiring measurement of rates as a function of pressure or synthesis of isotopically labeled substrates. Moreover, several recent studies indicate the results of such tests can prove ambiguous, as suggested by the footnotes in Table III. We therefore restrict our discussion primarily to the significance of ΔS^\ddagger values and buffer catalysis, since these formed the basis for the suggestion of an E_{1CB} mechanism by Walraevens et al. (26).

Significance of Activation Entropy. Saunders and Cockerill (9) suggested that activation entropy ΔS^\ddagger might be used to distinguish between E_2 and E_{1CB} mechanisms. The slow step in $(E_{1CB})_R$ and $(E_{1CB})_{ip}$ reactions involves halide ion elimination from a carbanion, a unimolecular process; in gas-phase reactions, such processes are frequently characterized by positive ΔS^\ddagger values. Conversely, the slow step in E_2 and $(E_{1CB})_I$ reactions involves a collision and formation of an activated complex between the base and the substrate, a bimolecular process that (again ignoring solvation effects) might be expected to give rise to negative ΔS^\ddagger values. Saunders and Cockerill (9) suggested that ΔS^\ddagger should be more negative for E_2 or $(E_{1CB})_I$ reactions in solution than for $(E_{1CB})_R$ reactions, but cautioned that this criterion's reliability had not been tested. Data for dehydrofluorination of pentahaloethanes (44) [$(E_{1CB})_R$ reaction] and $C_6H_5CHClCF_3$ (24) [$(E_{1CB})_{ip}$ mechanism] exhibit positive ΔS^\ddagger values of 50–100 J mol⁻¹ K⁻¹ in methanol solution, which might appear consistent with the predictions of Saunders and Cockerill (9). Other halogenated ethanes believed to react via $(E_{1CB})_{ip}$ mechanisms, such as $C_6H_5CHBrCF_2Br$, $C_6H_5CHClCF_2Cl$, p - $ClC_6H_4CHClCF_2Cl$, and $C_6H_5CHBrCH_2Br$, however, reveal smaller ΔS^\ddagger values in ethanol or methanol of -8 to 20 J mol⁻¹ K⁻¹ (23).

Activation parameters for base-promoted elimination reactions of chlorinated ethanes are summarized in Table IV. ΔH^\ddagger values for a given substrate generally agree closely; this rarely is the case with ΔS^\ddagger values, however, which display considerable scatter, reflecting their relatively small contribution to ΔG^\ddagger . Precise measurements of ΔS^\ddagger are notoriously difficult to obtain. Although error

Table IV. Activation Parameters for Base-Promoted Dehydrochlorination Reactions of Chlorinated Ethanes in Aqueous Solution^a

substrate	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	N^b	ref
ClH_2CCH_2Cl	82.4	-70 (120 °C)	2	45
$ClH_2CCH_2Cl^c$	93.8 ± 0.2	-40	5	26
$ClH_2CCH_2Cl^c$	95.0	-30	d	46
$H_3CCHCl_2^c$	110 ± 4	-20	5	27
$Cl_2HCCH_2Cl^e$	91.3 ± 0.2	10	5	26
$Cl_2HCCH_2Cl^c$	88 ± 17	-10	4	27
$ClH_2CCCl_3^c$	105 ± 1	40	6	26
$ClH_2CCCl_3^c$	98 ± 3	20	4	27
$Cl_2HCCHCl_2^c$	91.9 ± 0.3	60	4	26
$Cl_2HCCHCl_2$	89 ± 3	50	11	47
$Cl_2HCCHCl_2^c$	76 ± 2	3	4	27
$Cl_2HCCCl_3^c$	61.1 ± 0.4	-10	5	26
Cl_2HCCCl_3	79 ± 21 ^{e,f}	40	5	27
Cl_2HCCCl_3	75 ± 2	40	6	28
Cl_2HCCCl_3	78 ± 2 ^g	50	2	this study

^a Estimated error limits correspond to twice the estimated standard deviation unless otherwise noted. ^b Number of different temperatures at which reaction rates were measured. ^c Complete product information not provided; calculated activation parameters assume Arrhenius parameters correspond entirely to a single dehydrochlorination reaction. ^d Information not provided. ^e For reaction to 1,1-dichloroethylene. ^f One standard deviation. ^g Estimated error limits based on calculated uncertainty in second-order rate constants at each temperature.

limits on ΔS^\ddagger could be estimated from uncertainties in the intercepts of the Arrhenius plots, a more meaningful estimate of the uncertainty in ΔS^\ddagger can be approximated as $\sigma_{\Delta S^\ddagger} \approx \sigma_{\Delta H^\ddagger}/T$ (48). For the substrates in Table IV, such an estimation indicates relative errors in ΔS^\ddagger are often large, limiting the usefulness of ΔS^\ddagger as a diagnostic test of reaction mechanism.

The negative ΔS^\ddagger value computed for pentachloroethane by Walraevens et al. (26) stood out in contrast to the positive values they obtained for most other chlorinated ethanes, forming part of the reason why these researchers hypothesized (without further justification of their logic) that it might react via an E_{1CB} mechanism. Although our results, being based on measurements at only two temperatures, undoubtedly contain significant uncertainty, our estimated ΔS^\ddagger value of 50 J mol⁻¹ K⁻¹ is still substantially

different from the value of $-10 \text{ J mol}^{-1} \text{ K}^{-1}$ determined by Walraevens et al. (26). Moreover, it is virtually identical with ΔS^\ddagger values calculated from the results of Jeffers et al. (27) and Cooper et al. (28).

With the exception of the ΔS^\ddagger value reported for pentachloroethane by Walraevens et al. (26), the ΔS^\ddagger values in Table IV generally increase with increasing substrate chlorination. Of these substrates, pentachloroethane (which has the most acidic hydrogen) is the most likely to react via an $(E_{1CB})_R$ pathway, yet our isotope-exchange results prove otherwise. The majority of the ΔS^\ddagger values in Table IV are positive even though negative ΔS^\ddagger values might be expected for bimolecular reactions.

Most published studies of elimination mechanisms have been conducted with charged substrates in aqueous solution or neutral substrates in organic solvents. Solvation of neutral molecules by water is sufficiently different that the results of such experiments should be extrapolated with care to hydrophobic compounds in aqueous solution. We do not believe that positive ΔS^\ddagger values are inconsistent with an E_2 mechanism; both the apparent discrepancy between the positive ΔS^\ddagger measurements and anticipated values and the general increase in ΔS^\ddagger with chlorination can be explained as resulting from solvation. Smaller ions being more highly solvated in water than larger ions, there should be a greater increase in entropy in the activated complex $[\text{HO}\cdots\text{H}\cdots\text{C}(\text{R}^1\text{R}^2)\cdots\text{C}(\text{R}^3\text{R}^4)\cdots\text{Cl}]^-$ as chlorine is successively substituted for hydrogen in $\text{R}^1\text{--R}^4$, either for the transition state for an E_2 reaction or for the corresponding transition state for the first step of an $(E_{1CB})_I$ reaction. At the same time, S° values for the solvated ground-state substrate $\text{H--C}(\text{R}^1\text{R}^2)\text{--C}(\text{R}^3\text{R}^4)\text{Cl}$ should decrease with increasing substitution as more water molecules become organized around progressively larger solution cavities (49). The value of ΔS^\ddagger , which reflects the difference $S^\circ_{\text{transition state}} - (S^\circ_{\text{OH}^-} + S^\circ_{\text{substrate}})_{\text{ground state}}$, should thus increase with increasing chlorination, as observed. Although loss of translational and vibrational energy as two species interact to form an activated complex might tend to decrease entropy, inclusion of solvation effects can still result in positive ΔS^\ddagger values for bimolecular reactions. All of this suggests that the sign of the ΔS^\ddagger value may not reliably indicate whether reactions in aqueous solution occur via E_{1CB} mechanisms: citing a negative ΔS^\ddagger value in support of an E_{1CB} pathway appears tenuous.

Buffer Catalysis in Pentachloroethane Dehydrochlorination. The other factor leading Walraevens et al. (26) to suggest an E_{1CB} mechanism for pentachloroethane was the lack of observed general-base (buffer) catalysis in the presence of a phenolate buffer. With PhO^-/OH^- ratios from 10^3 to 10^4 , rates measured at 25°C were only 1–2 times the rate in the absence of phenolate (interpolated from measurements conducted at other temperatures). We have also observed a negligible effect with an even higher ratio of HS^-/OH^- (10^5) in our experiments with hydrogen sulfide/bisulfide buffers. This encouraged us to search for buffer catalysis in acid–base systems with lower $\text{p}K_a$ values.

Brønsted and Pedersen (50) noted that the kinetic reactivity of an acid or base buffer species could be related to its thermodynamic strength as an acid or base. For base-promoted processes such as bimolecular elimination mechanisms, the relationship takes the form

$$k_{B^-} = G(K_{HB})^{-\beta} \quad (4)$$

where k_{B^-} is the second-order rate constant for general-base catalysis by the base B^- , G is a constant for a given substrate, K_{HB} is the ionization constant for the acid HB , and the Brønsted coefficient β reflects the susceptibility of a given substrate to general-base catalysis. The parameter

β is often interpreted as indicating the extent of proton transfer between the substrate and the base in the transition state; its value should therefore lie between 0 and 1 (barring complications such as quantum-mechanical tunneling). Thus, for $(E_{1CB})_R$ and presumably for most $(E_{1CB})_{ip}$ reactions (assuming formation of ion pairs generally proceeds as a rapidly reversible preliminary equilibrium step), β should equal 1, whereas for $(E_{1CB})_I$ and E_2 mechanisms, β should be somewhat less than 1.

It can be difficult to observe buffer catalysis for substrates with high (or low) values of β . If the enhancement by a buffer constituent B^- of a base-promoted reaction is given by the ratio $(k_{B^-}(B^-))/(k_{\text{OH}^-}(\text{OH}^-))$ [ignoring any contribution from $k_{\text{H}_2\text{O}}(\text{H}_2\text{O})$], it can be shown (43) that this ratio is equal to

$$\frac{(k_{B^-}(B^-))}{(k_{\text{OH}^-}(\text{OH}^-))} = (\text{HB}) \left[\frac{K_{HB}}{K_W} \right]^{1-\beta} \quad (5)$$

For $(E_{1CB})_R$ or $(E_{1CB})_{ip}$ reactions with $\beta = 1$, concentrations of the acidic form of the buffer (HB) as high as 0.1 M would only produce a 10% rate enhancement. For smaller values of β , greater enhancement is predicted for higher ratios of K_{HB}/K_W . Although weaker bases are less effective than OH^- at removing protons, their greater abundance at low pH can more than compensate for their lesser reactivity. The lack of substantial catalysis by HS^- or PhO^- thus signifies a high value of β , but should not be taken to indicate an $(E_{1CB})_R$ or $(E_{1CB})_{ip}$ mechanism. Unfortunately, eq 5 cannot readily be applied to the buffer system studied by Walraevens et al. (26) to obtain an estimate for β , because the high buffer concentrations used by these investigators (0.9 M total phenol) violate the dilute solution approximations implicit in this expression.

Our studies with acetate buffers were designed to take advantage of eq 5; the ratio of ionization constants K_{HB}/K_W is as large as possible while still permitting reaction at a rate sufficiently rapid to measure. Our observations (Table II) do not allow us to determine a precise β value for this reaction, although we can set reasonable lower limits on β . If we assume that the true experimental error at this pH is equal to the 13% relative standard deviation we observed in second-order rate constants, then at the highest acetate concentration, a β value of 0.88 should produce a rate increase equivalent to 5 times our experimental error, while a β value of 0.85 should lead to a 10-fold increase in rate, relative to experimental error. Thus, the small or negligible effect of added acetate implies a high β value (>0.85).

An estimate for β can also be obtained from the experiments conducted in D_2O , based on knowledge of the relative acidities of HOD and DOD . For E_2 reactions at 25°C , $k_{\text{OD}^-}/k_{\text{OH}^-}$ values can be related (37) to β via the expression

$$k_{\text{OD}^-}/k_{\text{OH}^-} = 2.12^\beta \quad (6)$$

When our measurements in D_2O are used, this expression results in a β value of approximately 0.64; the accuracy of this estimate is very sensitive to errors in k_{OD^-} or k_{OH^-} .

Finally, estimates of β can also be obtained by comparing the rates of OH^- -promoted and neutral elimination reactions. In this case, applying eq 4 results in the expression

$$k_{\text{H}_2\text{O}}/k_{\text{OH}^-} = 10^{-15.74\beta} \quad (7)$$

In addition, the pH below which the neutral reaction predominates can be related to β by the expression

$$\text{pH}^* = 15.74(1 - \beta) \quad (8)$$

where pH^* is the pH at which $k_{\text{H}_2\text{O}}(\text{H}_2\text{O}) = k_{\text{OH}^-}(\text{OH}^-)$.

Table V. Calculated pH* and β Values for Polychlorinated Ethanes^a

substrate	pH*	β
H ₃ C ₃ C ₃ HCl ₂	12.48	0.21
ClH ₂ C ₃ C ₃ H ₂ Cl	<10.08	>0.36
ClH ₂ C ₃ C ₃ Cl ₃	8.08	0.49
Cl ₂ HC ₃ C ₃ H ₂ Cl	4.74	0.70
Cl ₂ HC ₃ C ₃ HCl ₂	4.51	0.71
Cl ₂ HC ₃ C ₃ Cl ₃	3.58	0.77

^aEstimates obtained from rates reported by Jeffers and co-workers (27, 46).

Extrapolating measurements of the rates of the neutral and base-promoted dehydrochlorination reaction of pentachloroethane reported by Jeffers et al. (27) to 25 °C, we can estimate values of β and pH* of 0.77 and 3.58, respectively.

Brønsted Coefficients for Other Polychlorinated Ethanes: Structure-Reactivity Implications. In addition to pentachloroethane, the results of Jeffers et al. (27) can be used to estimate β for other polychlorinated ethanes. Some caveats should however be noted in applying eq 7 or 8 to this data set. Complete product information was not generally provided (with the exception of pentachloroethane); other pathways such as substitution reactions may have contributed to observed rates. In most cases, substrate inertness required extrapolating results from higher temperatures to 25 °C. Nevertheless, this expression is relatively insensitive to errors in either second-order rate constant. Calculated values of β and pH*, summarized in Table V, reveal interesting trends. Increasing halogenation clearly produces increasing values of β , associated with lower pH* values below which the neutral reaction predominates. Chlorine substituents on C_β have a markedly greater impact on β than substituents on C_α. We can test whether the inductive effects of chlorine atoms as given by these β values contribute in an additive manner to the "acidity" of the hydrogen via a linear free-energy relationship. If we ignore steric effects, such a relationship might be given by the expression

$$\log_{10} (k_{\text{OH}^-}/k_{\text{H}_2\text{O}}) = 15.74\beta = \rho(n\sigma_{\beta\text{Cl}} + m\sigma_{\alpha\text{Cl}}) \quad (9)$$

where ρ represents the sensitivity of β values to inductive effects, n the number of chlorine atoms on C_β, and m the number of chlorine atoms on C_α. The parameters $\sigma_{\beta\text{Cl}}$ and $\sigma_{\alpha\text{Cl}}$ represent the inductive effects of a chlorine substituent on C_β and C_α, respectively. Applying a multiple regression to the limited set of data provided by 1,1-dichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and pentachloroethane results in estimated values of $\rho\sigma_{\beta\text{Cl}} = 4.54$ and $\rho\sigma_{\alpha\text{Cl}} = 1.16$ ($R^2 = 0.995$). That is, the inductive effect of a chlorine atom on C_β is nearly 4 times as great as that of a chlorine atom on C_α. This relative effect accords reasonably well with inductive constants obtained from the study of other systems. For example, for the polar substituent constant σ_1 (with σ_1 for H defined as 0), values are ~0 for CH₃, 0.17 for CH₂Cl, and 0.46 for Cl (51). For the polychlorinated ethanes in Table V, these inductive effects are primarily expressed through k_{OH^-} values, which tend to increase dramatically with increasing halogenation.

Implications for Experimental Determination of Dehydrohalogenation Kinetics. Recent investigations (e.g., ref 47) have conducted dehydrohalogenation experiments at high (0.1 M) buffer concentrations. Such systems certainly present advantages in terms of ease of obtaining stable pH measurements, but they raise the question of whether the results are subject to error because

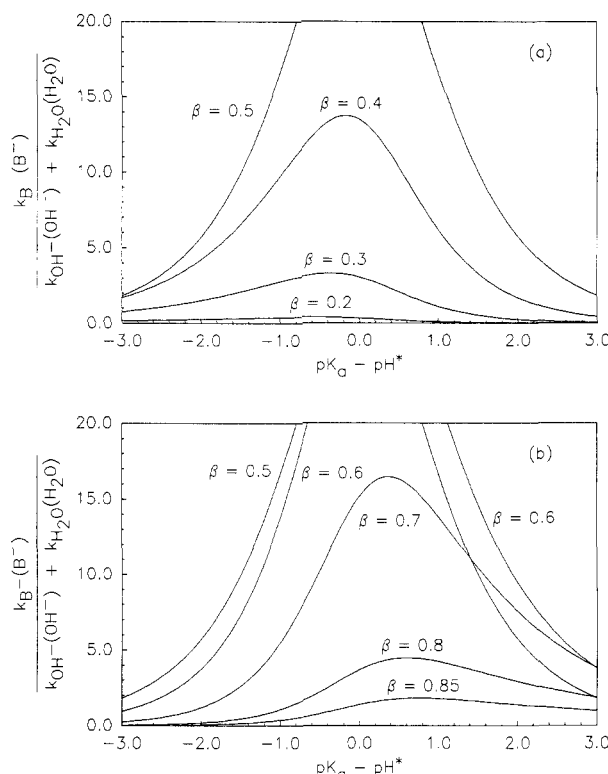


Figure 6. Theoretical contribution of buffer catalysis to dehydrohalogenation rates measured in buffer systems of varying pK_a as a function of substrate pH* and β . Calculations assume pH of experimental system equals buffer pK_a , with total buffer concentration of 0.10 M; (a) $\beta \leq 0.5$; (b) $\beta \geq 0.5$.

of unrecognized buffer catalysis. For any dehydrohalogenation experiment, the total rate will be the sum of the contributions from the OH⁻-promoted, the buffer-promoted, and the neutral reaction, i.e.:

$$\text{observed rate} = k_{\text{OH}^-}(\text{OH}^-) + k_{\text{B}}(\text{B}^-) + k_{\text{H}_2\text{O}}(\text{H}_2\text{O}) \quad (10)$$

The relative magnitudes of these terms can be estimated for any system for a given pH and buffer concentration from the Brønsted relationship. If we assume experiments are conducted at a pH equal to the pK_a of the buffer acid-base system, we can plot the contribution of the $k_{\text{B}}(\text{B}^-)$ term for various values of β as a function of the difference between the pH of the experiment (the pK_a of the buffer) and the pH* value of the substrate, as shown in Figure 6. Our calculations indicate that buffer catalysis is most likely to be important in an experiment at pH values near the pH* value, especially for substrates with intermediate values of β . At higher pH, the greater ratio of OH⁻ to the conjugate base of the buffer salt makes significant buffer catalysis less likely, especially as β increases, while at lower pH, the much greater abundance of H₂O will cause the $k_{\text{H}_2\text{O}}(\text{H}_2\text{O})$ term to dominate the rate expression, particularly for substrates with small values of β .

Such an analysis may explain the results of Burlinson et al. (52), who noted that different buffers varied in their ability to catalyze the dehydrohalogenation of 1,2-dibromo-3-chloropropane. For this substrate, we can estimate β and pH* values at 25 °C of 0.6 and 6.9 from their data obtained at other temperatures. With this β value, 1,2-dibromo-3-chloropropane should be more susceptible to general-base catalysis by buffers with a pK_a near 6.9 than by buffers with substantially higher or lower pK_a values. Observations of catalysis in experiments conducted at pH 6.8–6.9 with H₂PO₄⁻/HPO₄²⁻ buffers ($pK_a \approx 7$), but not with H₃BO₃/H₂BO₃⁻ buffers ($pK_a \approx 9$) at pH 8.9, or

with phthalate buffers ($pK_{a1} \approx 3$, $pK_{a2} \approx 5$) at pH 4, agree qualitatively with these predictions.

Conclusions with Respect to Pentachloroethane Reaction Mechanism. In terms of understanding the mechanism of pentachloroethane dehydrochlorination, the values estimated for the Brønsted coefficient β indicate a high degree of proton transfer in the transition state. Although we cannot rule out an $(E_{1CB})_I$ or an $(E_{1CB})_{ip}$ pathway from the available data, we still believe the most likely mechanism is the concerted E_2 reaction, albeit via a transition state with considerable E_{1CB} character in the context of a variable transition-state model. If any substrate reacts via a concerted mechanism, then the simple chlorinated alkanes of Table IV certainly represent likely candidates. The absence of any abrupt change in activation parameters for pentachloroethane (Table IV) might indicate a common reaction mechanism, although uncertainties in many of the available measurements somewhat weaken this argument.

Additional evidence in favor of an E_2 mechanism is provided by comparing the kinetics of pentachloroethane dehydrochlorination with rates of proton exchange for chloroform and 1,1,1-trifluoro-2,2-dichloroethane. In the case of an E_{1CB} mechanism for pentachloroethane, the rate of proton removal (k_1 in Figure 2b) ought to be similar for all three substrates, under the reasonable assumption that these are dominated by inductive effects. Using a deprotonation rate extrapolated from $CDCl_3$ reaction with OH^- in H_2O of $0.202\ M^{-1}\ s^{-1}$ (14), and applying the primary hydrogen isotope effect of 1.42 (43), we can estimate a rate for the deprotonation of $CHCl_3$ by OH^- in H_2O of $0.29\ M^{-1}\ s^{-1}$ at $25\ ^\circ C$. Available data are insufficient to provide as precise an estimate of the rate of $CHCl_2CF_3$ deprotonation in H_2O , but an approximate rate of $\sim 0.2\ M^{-1}\ s^{-1}$ for this reaction can be obtained from data for $CDCl_2CF_3$ in methanol (19), noting that $CHCl_2CF_3$ proton transfer in D_2O at $0\ ^\circ C$ is 10 times faster than $CDCl_2CF_3$ deuterium exchange in methanol at the same temperature. If pentachloroethane were to react via any E_{1CB} mechanism, then the overall rate of dehydrochlorination could not be any faster than the rate of this first step in the reaction sequence. That pentachloroethane's reaction is 2 orders of magnitude faster than the rates of proton exchange for chloroform and 1,1,1-trifluoro-2,2-dichloroethane suggests that some other factor, such as partial double-bond formation accompanied by partial carbon-chlorine bond breakage, is stabilizing the transition state.

Implications for Hexachloroethane Transformation. Our results indicate that pentachloroethane undergoes dehydrochlorination via a bimolecular, pH-dependent reaction at a rate that is rapid relative to other polychlorinated ethanes. Although we cannot prove this transformation occurs via a concerted E_2 mechanism, we can rule out a stepwise $(E_{1CB})_R$ mechanism and can discount an $(E_{1CB})_{ip}$ mechanism in which reprotonation to revert to the starting material is much more rapid than halide ion elimination to yield tetrachloroethylene. Thus, pentachloroethane occasionally reported from the reduction of hexachloroethane is not likely to result from protonation of a free pentachloroethyl carbanion, but rather is almost certainly produced by hydrogen atom abstraction by a pentachloroethyl radical. This may be true even for intermediates stabilized as organometallic complexes in the active sites of enzymes. On the basis of electron donor mass balances, Nastainczyk et al. (7) concluded that all of the pentachloroethane they observed during the reduction of hexachloroethane by cytochrome P-450 in rat liver microsomal preparations resulted from H^\bullet abstraction

by a pentachloroethyl radical rather than via carbanion protonation. Production of pentachloroethane thus might prove useful as a diagnostic feature for free radical as opposed to two-electron mechanisms for hexachloroethane reduction.

Because pentachloroethane dehydrochlorination to tetrachloroethylene may be rapid, any study of hexachloroethane reduction mechanisms needs to address the possibility that pentachloroethane might represent a reaction intermediate. This is particularly true for experiments conducted at high pH or for experiments conducted at neutral pH if hexachloroethane reduction is relatively slow. Depending on the relative rates of hexachloroethane and pentachloroethane transformation to tetrachloroethylene, even minor amounts of pentachloroethane may signify a role as a reaction intermediate rather than a side product. In such a case, the reduction of hexachloroethane to tetrachloroethylene (rapidly becoming entrenched in the environmental chemistry literature as an example of reductive elimination) might even prove to occur to a significant extent via the entirely incidental dehydrochlorination reaction of pentachloroethane. Studies we have conducted investigating the reduction of hexachloroethane by microorganisms under reducing conditions in groundwater (8) revealed traces of pentachloroethane, absent in poisoned controls. Consideration of the relative rates of hexachloroethane and pentachloroethane transformation indicates that even though measured concentrations of pentachloroethane were very low, a significant fraction of the transformation pathway—on the order of 20–30% or more—could still be proceeding via a pentachloroethane intermediate. Our results should provide parameters needed by future studies to further address this issue.

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Registry No. Cl_2CHCCl_3 , 76-01-7; $Cl_2C=CCl_2$, 127-18-4.

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