is chain end initiation from vinylidene chain ends. The most stable reaction is random scission initiation within the polymer chains. At a heating rate of 2 °C/min, the peak temperature of each reaction in the DTG curve is about 165, 270, and 360 °C, respectively.

2. Chain-transfer agents used in the polymerization process apparently significantly reduce the number of H–H linkages and vinylidene ends and thereby stabilize radically polymerized PMMA.

3. The different initiators used in this study, AIBN and BPO, do not produce significant differences in the thermal and oxidative degradation of PMMA. Also, phenyl radical initiated polymer chains and benzoyloxy radical initiated polymer prepared with BPO do not cause any significant difference in the thermal and oxidative degradation of PMMA.

4. Gas-phase oxygen very effectively traps radicals originating from chain scissions at the H–H linkages. Similarly, oxygen also traps some of radicals generated by end initiation. However, this trapping by oxygen is not as effective as that for the H–H linkage.

Acknowledgment. We thank Dr. Wing Tsang at NBS for his valuable discussions and suggestions regarding degradation chemistry.

Registry No. PMMA (homopolymer), 9011-14-7.

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Tri-*n*-butyltin Hydride Reduction of Poly(vinyl chloride): Kinetics of Dechlorination for 2,4-Dichloropentane and 2,4,6-Trichloroheptane

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ABSTRACT: 2,4-Dichloropentane (DCP) and 2,4,6-trichloroheptane (TCH) were reductively dechlorinated with tri-*n*-butyltin hydride ((*n*-Bu)$_3$SnH) directly in the NMR sample tube. Carbon-13 NMR spectra were recorded periodically to monitor the progress of DCP and TCH dechlorination. From these observations the following kinetic conclusions were drawn: (i) meso (*m*) DCP was reduced 30% faster than racemic (*r*) DCP; (ii) the Cl from DCP was removed 4 times faster than the Cl in 2-chloropentane or 2-chlorooctane; (iii) the 4-Cl in *mm*-TCH is removed faster than the 4-Cl in *mr*-TCH, which in turn is more reactive than the 4-Cl in the *rr* isomer; and (iv) the 4-Cl in TCH is removed 1.5 times faster than the 2- or 6-Cl's. Conclusions i and ii were previously observed at the diad level, at least qualitatively, in the (*n*-Bu)$_3$SnH reduction of poly(vinyl chloride) (PVC) to ethylene–vinyl chloride (E–V) copolymers. With the kinetic information obtained from the reduction of DCP and TCH, an attempt was made to simulate the (*n*-Bu)$_3$SnH reduction of PVC to E–V copolymers. Comparison of the structures of the E–V copolymers simulated on the computer with those determined for (*n*-Bu)$_3$SnH-reduced PVC by ^{13}C NMR permits us to conclude that DCP and TCH are model compounds appropriate for studying the reductive dechlorination of PVC.

Introduction

Tri-*n*-butyltin hydride ((*n*-Bu)$_3$SnH) has been used to reductively dechlorinate poly(vinyl chloride) (PVC) to polyethylene (PE) during the course of studying the microstructure of PVC.[1] The structure of the starting PVC is deduced from that of the PE resulting from its complete dechlorination. Partial reduction of PVC with (*n*-Bu)$_3$SnH has also produced a series of ethylene–vinyl chloride (E–V) copolymers. ^{13}C NMR analysis of these E–V copolymers has revealed the details of their microstructures.[2]

This series of E–V copolymers, which is not possible to obtain either by copolymerization of E and V monomers or by chlorinating PE, was found to have the same chain length as the starting PVC. As the amount of Cl removed was increased, it was observed that the ratio of racemic

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0024-9297/86/2219-2168$01.50/0

(r) to meso (m) VV diads increased, and the disappearance of VV diads was greater than anticipated for the random removal of Cl's. Consequently, we concluded from the $(n\text{-Bu})_3$SnH reduction of PVC to E–V copolymers and eventually to PE that Cl's belonging to VV diads are preferentially removed relative to isolated Cl's (EVE) and that m-VV diads are reduced faster than r-VV diads.

Subsequent studies of the physical properties of this series of E–V copolymers obtained via the $(n\text{-Bu})_3$SnH reduction of PVC have revealed that their properties, both in the solid state and in solution, are sensitive to their detailed microstructure.[3-6] These observations prompted the present study concerning the mechanisms of the reductive dechlorination of PVC with $(n\text{-Bu})_3$SnH.

We have chosen the PVC diad and triad compounds 2,4-dichloropentane (DCP) and 2,4,6-trichloroheptane (TCH) as subjects for our attempt to obtain quantitative kinetic data characterizing their $(n\text{-Bu})_3$SnH reduction in the hope that they will serve as useful models for the reduction of PVC to E–V copolymers. Unlike the polymers (PVC and E–V), DCP and TCH are low molecular weight liquids whose high-resolution ^{13}C NMR spectra can be recorded from their concentrated solutions in a matter of minutes. Thus, it is possible to monitor their $(n\text{-Bu})_3$SnH reduction directly in the NMR tube and follow the kinetics of their dechlorination.

Finally the kinetic data are compared to the microstructures of the E–V copolymers obtained by $(n\text{-Bu})_3$SnH reduction of PVC to test the suitability of DCP and TCH as model compounds for PVC reduction. This is achieved by computer modeling the reduction of PVC to E–V copolymers with the aid of the kinetic parameters obtained from the study of DCP and TCH reduction and then comparing the observed and modeled E–V microstructures.

Experimental Section

Materials. The 2-chloro-4-methylpentane, 2-chlorooctane, and 4-chlorooctane were purchased from Wiley Organics and used as received. The 2,4-dichloropentane was obtained from Pfaltz & Bauer and also used as received. Tri-n-butyltin hydride (Alfa Division, Ventron Corp.) was vacuum-distilled and stored under argon before use. The free radical initiator azobis(isobutyronitrile) (AIBN) used in the reduction was also purchased from Alfa Division. The 2,4,6-trichloroheptane was obtained from a new synthesis which involves the hydrohalogenation of 1,6-heptadien-4-ol and the chlorination of the resulting alcohol. A detailed description of this method can be found elsewhere.[7]

Sample Preparation. In a small vial 22.5 mg of AIBN was mixed with 1.7 mL of perdeuteriobenzene and the mixture was held at 0 °C to permit dissolution of the AIBN. The chloroalkane and 0.2 mL of the NMR reference material hexamethyldisiloxane (HMDS) were placed in a 10-mm NMR tube. The AIBN/benzene solution was added to the NMR tube and placed under an argon atmosphere in a glovebag. The freshly distilled $(n\text{-Bu})_3$SnH (1.0–1.7 mL) was transferred by syringe into the solution. Following a thorough mixing, the sample was degassed with argon for several minutes and sealed with paraffin film. The amount of chlorinated alkane varied between 0.2 and 0.4 mL (7.0–12.5% (v/v)), and the $(n\text{-Bu})_3$SnH added was equal to the molar concentration of chlorine atoms present. The sample was placed in the NMR spectrometer at 50 °C, and the ^{13}C NMR spectra were recorded as the reduction proceeded.

NMR Measurements. Initially, the reduction of 2-chloro-4-methylpentane was carried out in order to ascertain the ideal temperature which would lead to complete reduction in about 6 h. The progress of this reduction was followed by ^{1}H NMR, recording a single scan every 30 min. It was found that at 50 °C the reaction reaches 80% of completion after 5 h. All subsequent reductions were carried out at this temperature.

The 50.31-MHz ^{13}C NMR spectra of the chlorinated alkanes were recorded on a Varian XL-200 NMR spectrometer. The temperature for all measurements was 50 °C. It was necessary to record 10 scans at each sampling point as the reduction proceeded. A delay of 30 s was employed between each scan. In order to verify the quantitative nature of the NMR data, carbon-13 T_1 data were recorded for all materials using the standard 180°–τ–90° inversion–recovery sequence. Relaxation data were obtained on $(n\text{-Bu})_3$SnH, $(n\text{-Bu})_3$SnCl, DCP, TCH, pentane, and heptane under the same solvent and temperature conditions used in the reduction experiments. In addition, relaxation measurements were carried out on partially reduced (70%) samples of DCP and TCH in order to obtain T_1 data on 2-chloropentane, 2,4-dichloroheptane, 2,6-dichloroheptane, 4-chloroheptane, and 2-chloroheptane. The results of these measurements are presented in Table I. In the NMR analysis of the chloroalkane reductions, we measured the intensity of carbon nuclei with T_1 values such that a delay time of 30 s represents at least $3T_1$. The only exception to this is heptane, where the shortest T_1 is 12.3 s (delay = $2.5T_1$). However, the error generated would be less than 10%, and, in addition, heptane concentration can also be obtained by product difference measurements in the TCH reduction. Measurements of the nuclear Overhauser enhancement (NOE) for carbon nuclei in the model compounds indicate uniform and full enhancements for those nuclei used in the quantitative measurements. Table I also contains the chemical shift data for all compounds studied. The chemical shift data for the TCH sample agree well with those of an earlier report where the shift assignment of each stereoisomer was established.[8] The percent reduction was determined by comparing the amounts of $(n\text{-Bu})_3$SnH and $(n\text{-Bu})_3$SnCl at each measurement point.

Kinetics of $(n\text{-Bu})_3$SnH Reduction of DCP and TCH

DCP Reduction. As illustrated below DCP (D) is sequentially transformed into 2-chloropentane (M) and then to pentane (P) during its reduction with $(n\text{-Bu})_3$SnH.

$$\mathrm{D} \xrightarrow{k_D} \mathrm{M} \xrightarrow{k_M} \mathrm{P}$$

The ratio of rate constants $K = k_M/k_D$ can be obtained[9] from the concentrations of D and M measured at various degrees of reduction x according to

$$\frac{M_x}{D_x} = \frac{1 - (D_x/D_0)^{K-1}}{K - 1} \tag{1}$$

where the subscripts "0" and "x" indicate concentrations initially and after percent reduction x.

An alternative means to determine the relative rates of reduction of M and D, i.e., $K = k_M/k_D$, is afforded by comparing the simultaneous $(n\text{-Bu})_3$SnH reductions of DCP and 2-chlorooctane (M′) to pentane and octane (O), respectively.

$$\mathrm{D} \xrightarrow{k_D} \mathrm{M} \xrightarrow{k_M} \mathrm{P}$$

$$\mathrm{M}' \xrightarrow{k_{M'}} \mathrm{O}$$

In this case $K' = k_{M'}/k_D$ is given by[9]

$$K' = \frac{\ln (M_x'/M_0')}{\ln (D_x/D_0)} \tag{2}$$

Equation 2 can also be used to determine the relative rates of reduction of meso (m) and racemic (r) DCP (D_m, D_r) where M′ and D are replaced by D_m and D_r.

$$D_m \xrightarrow{k_{D_m}} \mathrm{M} \xrightarrow{k_M} \mathrm{P}$$

$$D_r \xrightarrow{k_{D_r}} \mathrm{M} \xrightarrow{k_M} \mathrm{P}$$

TCH Reduction. In the early stages of the reduction of TCH (T) with $(n\text{-Bu})_3$SnH, it is possible to compare the relative reactivities of the central (4) and terminal (2, 6) chlorines. At these levels of reduction only 2,6- and 2,4-

Table I
^{13}C NMR Spin-Lattice Relaxation Times (T_1) and Chemical Shifts (δ)

structure	δ	T_1, s
H-Sn(C-C-C-C)$_3$ (a b c d)	a, 8.30	6.0
	b, 27.41	8.5
	c, 30.24	7.3
	d, 13.82	8.1
Cl-Sn(C-C-C-C)$_3$ (a b c d)	a, 17.53	4.5
	b, 27.04	7.0
	c, 28.19	5.9
	d, 13.64	7.3
Cl Cl (m,r) C-C-C-C-C (a b c)	a, 25.50 (*r*)	6.7
	a, 24.49 (*m*)	6.4
	b, 55.38 (*r*)	15.7
	b, 54.24 (*m*)	15.8
	c, 50.86 (*r*)	8.9
	c, 50.51 (*m*)	8.8
Cl C-C-C-C-C (a b c d e)	a, 25.41	9.0
	b, 57.58	21.8
	c, 42.82	13.3
	d, 20.06	14.8
	e, 13.56	
C-C-C-C-C (a b c)	a, 14.12	10.8
	b, 22.62	24.6
	c, 34.46	24.4
Cl Cl Cl (m,r) (m,r) C-C-C-C-C-C-C (a b c d)	a, 25.34 (*rr*)	3.5–3.7
	a, 24.21 (*mr, rm*)	
	a, 24.11 (*mm*)	
	b, 55.19 (*rr*)	8.1–8.4
	b, 55.07 (*mr*)	
	b, 54.14 (*rm*)	
	b, 53.93 (*mm*)	
	c, 49.02 (*rr*)	4.4–4.6
	c, 48.84 (*mr*)	
	c, 48.33 (*rm*)	
	c, 47.81 (*mm*)	
	d, 58.32 (*rr*)	8.2
	d, 57.44 (*mr, rm*)	8.1
	d, 56.39 (*mm*)	8.0
Cl Cl (m,r) C-C-C-C-C-C-C (a b c d e f g)	a, 25.59 (*r*)	
	a, 23.50 (*m*)	
	b, 55.56 (*r*)	
	b, 54.41 (*m*)	
	c, 49.30 (*r, m*)	
	c, 48.55	
	d, 60.51 (*r*)	
	d, 59.58 (*m*)	
	e, 41.10 (*r, m*)	
	e, 40.07	
	f, 19.76 (*r, m*)	
	f, 19.61	
	g, 14.07 (*r, m*)	12.4
Cl Cl (m,r) C-C-C-C-C-C-C (a b c d)	a, 25.33 (*r, m*)	~5.7
	a, 25.30	
	b, 57.80 (*r, m*)	~11.0
	c, 40.07 (*r, m*)	6.4
	c, 40.02	
	d, 24.10 (*r, m*)	~3.6
	d, 24.02	
Cl C-C-C-C-C-C-C (a b c d)	a, 14.07	12.4
	b, 19.96	8.9
	c, 41.01	6.3
	d, 63.08	
Cl C-C-C-C-C-C-C (a b c d e f g)	a, 25.40	5.7
	b, 58.25	14.6
	c, 40.71	7.2
	d, 26.60	8.5
	e, 31.64	9.3
	f, 22.80	10.5
	g, 14.20	12.3
C-C-C-C-C-C-C (a b c d)	a, 14.20	12.3
	b, 23.01	13.2
	c, 32.24	12.3
	d, 29.35	12.4

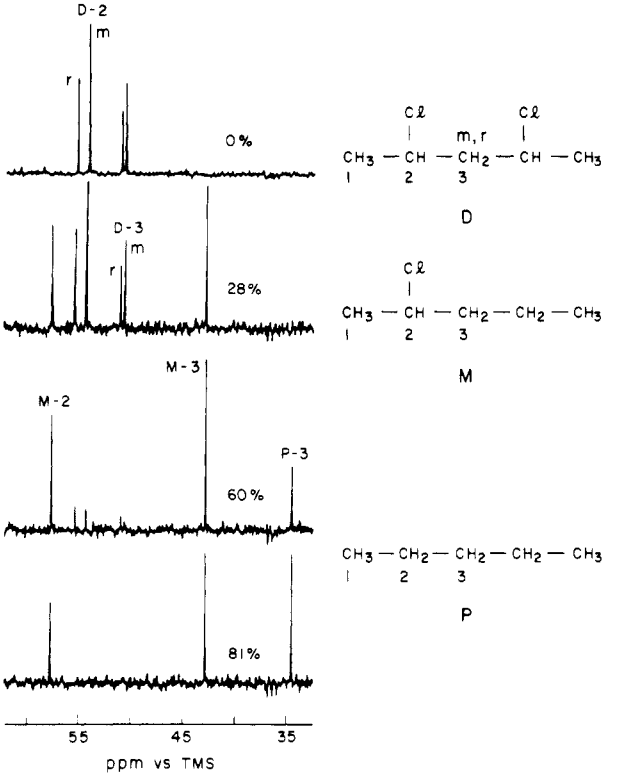

Figure 1. 50.31-MHz ^{13}C NMR spectra of DCP (D) and its products (M and P) resulting from 0, 28, 60, and 81% reduction with $(n\text{-Bu})_3$SnH.

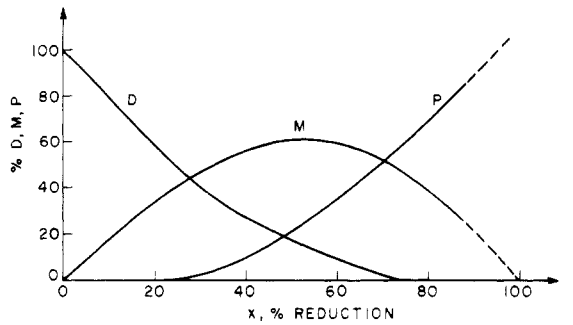

Figure 2. Distribution of reactants (D, M) and products (M, P) observed in the $(n\text{-Bu})_3$SnH reduction of DCP. D = DCP, M = 2-chloropentane, and P = pentane (See Figure 1).

dichloroheptanes (2,6-D and 2,4-D) are produced, as shown below.

$$T \xrightarrow{k_C} 2,6\text{-D}$$

$$T \xrightarrow{k_E} 2,4\text{-D}$$

We can establish the relative reactivities, k_C/k_E, of the central (C) and terminal (E) chlorines directly from the relative concentrations of the resulting dichloroheptanes.

$$\frac{k_C}{k_E} = \frac{2,6\text{-}D}{2,4\text{-}D} \tag{3}$$

Results and Discussion

Kinetic Results for DCP and TCH. The portion of the 50.31-MHz ^{13}C NMR spectra containing the methylene and methine carbon resonances of DCP and the resultant products of its $(n\text{-Bu})_3$SnH reduction are presented in Figure 1 at several degrees of reduction. Comparison of the intensities of resonances possessing similar T_1 relaxation times (see above) permits a quantitative accounting

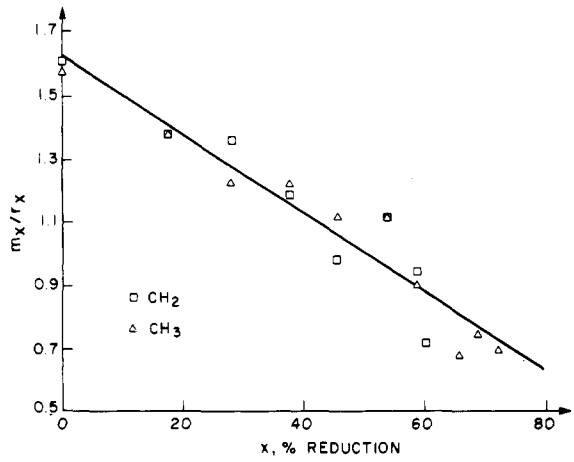

Figure 3. Ratio of the relative amounts of *m* and *r* isomers of DCP remaining after reduction by $(n\text{-Bu})_3\text{SnH}$, as measured by the carbon-13 methylene (see Figure 1) and methyl resonances.

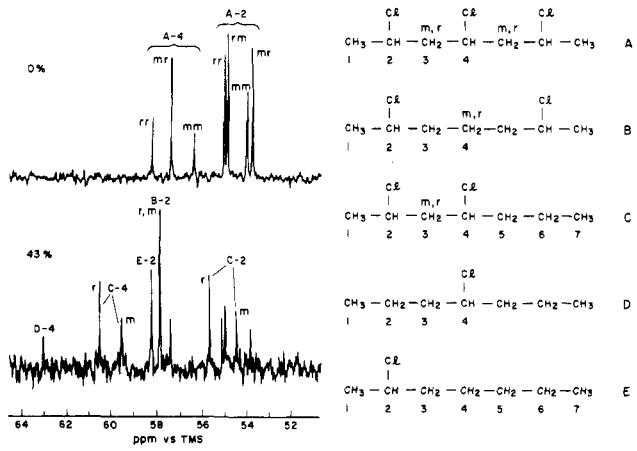

Figure 4. Methine carbon region of the 50.31-MHz ^{13}C NMR spectra of TCH at 0 and 43% reduction with $(n\text{-Bu})_3\text{SnH}$.

of the amounts of each species (D, M, and P) present at any degree of reduction.

In Figure 2 the percentages of D (DCP), M (2-chloropentane), and P (pentane) observed during the $(n\text{-Bu})_3\text{SnH}$ reduction of DCP are plotted against the degree of reduction *x*. Equation 1 is solved for $K = k_M/k_D$ by least-squares fitting the calculated and observed values of the ratio (M_x/D_x). The observed ratios (D_x/D_0) are substituted into eq 1 to obtain the calculated ratios (M_x/D_x) corresponding to the assumed $K = k_M/k_D$, and these are compared with the observed ratios (M_x/D_x). This procedure yields $K = k_M/k_D = 0.26$, which means that DCP is ~4 times more easily reduced than 2-chloropentane. Comparison of the simultaneous reduction of DCP and 2-chlorooctane gave $K' = k_{M'}/k_D = 0.24$ according to eq 2, lending further support to the observation that chlorines belonging to a VV diad are removed 4 times faster than an isolated chlorine in, say, an EVE triad. Furthermore, the observed rates of $(n\text{-Bu})_3\text{SnH}$ reductions of 2- and 4-chlorooctanes were identical within experimental error. This means that the reactivity of an isolated chlorine is independent of structural position or chain-end effects.

The observed ratios of *m* to *r* isomers, m_x/r_x, remaining during the $(n\text{-Bu})_3\text{SnH}$ reduction of DCP (see Figure 1) are plotted in Figure 3. Substituting these data into eq 2 yields a ratio of $k_{D_m}/k_{D_r} = 1.3$. Apparently *m*-VV diads are 30% more reactive toward $(n\text{-Bu})_3\text{SnH}$ than are *r*-VV diads.

Our ^{13}C NMR analysis[2] of the E–V copolymers obtained via the $(n\text{-Bu})_3\text{SnH}$ reduction of PVC led to $k_m/k_r = 1.31$

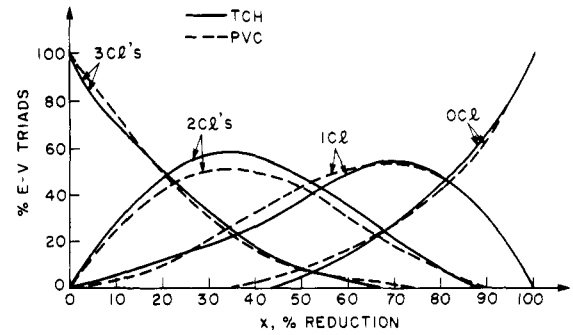

Figure 5. Comonomer triad distributions observed by ^{13}C NMR analysis during the $(n\text{-Bu})_3\text{SnH}$ reductions of TCH (—) and PVC (– – –).

Table II
Relative Reactivities of the Central Chlorines in E–V Triads

E–V triad	–	reduction site	+	*k* (rel)
EEE	0	0	0	0.0
EVE	0	1	0	1.0
r-EVV	0	1	1	3.5
m-EVV	0	1	1	4.6
mr-VVV	1	1	1	4.0 × 1.5 = 6.0
rr-VVV	1	1	1	6.0 ÷ 1.3 = 4.6
mm-VVV	1	1	1	6.0 × 1.3 = 7.8

± 0.1., in excellent agreement with the kinetics observed for the removal of chlorines from *m*- and *r*-DCP. We also found no VV diads in those E–V copolymers made by removing more than 80% of the chlorines from PVC. This observation is confirmed in the $(n\text{-Bu})_3\text{SnH}$ reduction of DCP where the chlorines in this PVC diad model compound were found to be 4 times easier to remove than the isolated chlorines in 2-chloropentane, 2-chlorooctane, and 4-chlorooctane.

The ^{13}C NMR spectra of TCH before and after 43% reduction with $(n\text{-Bu})_3\text{SnH}$ are shown in Figure 4. The shift assignments given in the figure, and those listed in Table I were obtained by comparison to the chemical shift data of TCH, DCP, and 2- and 4-chlorooctanes. From the relative concentrations of 2,6- and 2,4-dichloroheptane (2,6-D and 2,4-D) observed in the early stages of TCH reduction with $(n\text{-Bu})_3\text{SnH}$ we determine according to eq 3 that the reactivity of the central chlorine in TCH is 50% greater than that of the terminal chlorines; i.e., $k_C/k_E = 1.5$. We also find the reactivity of the central chlorine in TCH to depend on its stereoisomeric environment as follows: *mm* > *mr* or *rm* > *rr*.

In Figure 5 we have plotted and compare the triad sequences observed in the reduction of TCH and PVC with $(n\text{-Bu})_3\text{SnH}$. The curves numbered 0, 1, 2, and 3 correspond to triads containing 0 (EEE), 1 (VEE + EEV + EVE), 2 (VVE + EVV + VEV), and 3 (VVV) chlorine atoms. There is agreement between the curves describing the products of reduction for TCH and PVC, providing strong support for considering TCH an appropriate model compound for the $(n\text{-Bu})_3\text{SnH}$ reduction of PVC. This clearly implies that the $(n\text{-Bu})_3\text{SnH}$ reduction of PVC is independent of comonomer sequences longer than triads.

The first column of Table II lists all possible ^{13}C NMR distinguishable E–V triads whose central units are V. In the next column we present the same triad structures in binary notation (0 = E, 1 = V), with the central unit labeled as the site of $(n\text{-Bu})_3\text{SnH}$ attack and the terminal units as either "–" (preceding site) or "+" (following site). The final column presents the relative reactivities of the central V (1) unit in each triad toward $(n\text{-Bu})_3\text{SnH}$ based on the kinetics of reduction determined for DCP and TCH.

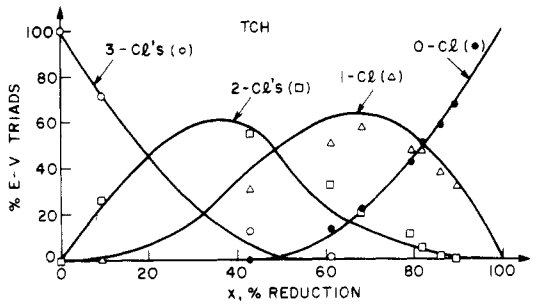

Figure 6. Comparison of the observed (symbols) and simulated (solid lines) comonomer triad distributions in $(n\text{-Bu})_3$SnH-reduced TCH.

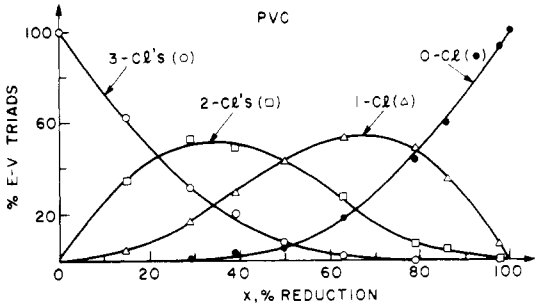

Figure 7. Comparison of the observed (symbols) and simulated (solid lines) comonomer triad distributions in $(n\text{-Bu})_3$SnH-reduced PVC.

For the EVV (011) triads, removal of the central chlorine atoms is expected to be 3.5 (*r*) and 4.6 (*m*) times faster than for the isolated chlorine atom in the EVE (010) triad, because $k_D/k_M = 4.0$ and $k_{D_m}/k_{D_r} = 1.3$ for DCP. The central chlorines in VVV (111) triads are 6.0 (*mr* or *rm*), 4.6 (*rr*), and 7.8 (*mm*) times more reactive toward $(n\text{-Bu})_3$SnH than the chlorine in the EVE triad based on $k_D/k_M = 4.0$ and $k_{D_m}/k_{D_r} = 1.3$ for DCP and $k_C/k_E = 1.5$ for TCH.

Computer Simulation of TCH and PVC Reduction. We begin with 100 TCH molecules reflecting the stereochemical composition of our unreduced TCH sample, i.e., 52 (*mr* or *rm*), 28 (*rr*), and 20 (*mm*) stereoisomers. A TCH molecule is selected by generating a random integer, I_r, where $1 < I_r < 100$. If $1 < I_r < 52$, then the TCH molecule chosen is an *mr* or *rm* isomer. If $53 < I_r < 80$, then the TCH is *rr*, and if $I_r > 80$ the TCH selected is an *mm* isomer.

Next we randomly choose either one or the other terminal units or the central unit of our selected TCH isomer and check to see if it is a V (1) unit or an E (0) unit. If a terminal V unit is chosen, we check to see if the neighboring central unit is V or E. If the central unit is also V,[10] then we determine whether this VV diad is *m* or *r*. For *r*- and *m*-VV diads the relative reactivities of the terminal V unit chlorine are 3.5 and 4.6, respectively (see Table II). Finally, we select a random number between 0.0 and 1.0. If it is smaller than the relative reactivity divided by the sum of the relative reactivities of all chlorines in the VVV, EVV or VVE, VEV, VEE or EEV, and EVE isomers of TCH and partially reduced TCH (see Table II), then we remove the terminal chlorine (1 → 0) and modify the relative reactivity of the central V unit in the selected TCH isomer, because its terminal neighbor has been changed from V to E.

This procedure is repeated until the desired percent reduction, *x*, is reached, where $x = 100 \times$ (no. of chlorines removed ÷ 300). Each of the 100 TCH molecules is then tested for the number and sequence of V units remaining at this current value of *x*. In Figure 6 we plot the percent TCH molecules containing 3, 2, 1, and 0 chlorines, or V units, determined from our simulation and compare them to [redacted] values observed for TCH at various degrees of $(n\text{-Bu})_3$SnH reduction. Agreement between the simulated and observed reduction products of TCH based on the kinetics observed for both DCP and TCH is good.

Simulation of the $(n\text{-Bu})_3$SnH reduction of PVC is carried out in a manner similar to that described for TCH. Instead of beginning with 100 TCH molecules, we take a 1000 repeat-unit PVC chain that has been Monte Carlo generated to reproduce the stereosequence composition of the experimental sample of PVC used in the reduction to E–V copolymers,[2] i.e., a Bernoullian PVC with $P_m = 0.45$. At this point we have generated a PVC chain with a chain length and a stereochemical structure that matches our experimental starting sample of PVC.

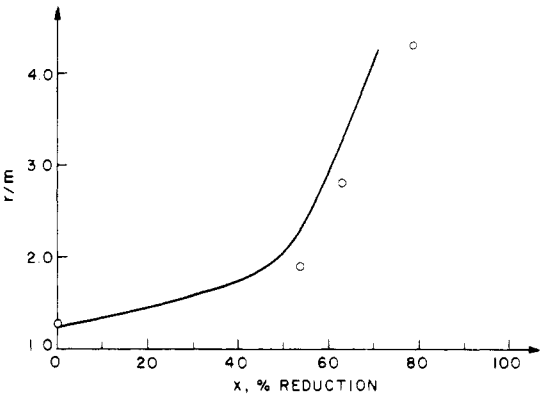

Figure 8. Comparison of the observed (○) and simulated ratios of *r*/*m* VV diads during the $(n\text{-Bu})_3$SnH reduction of PVC.

We select repeat units at random, and if they are unreduced V units a check of whether or not the units adjacent to the selected unit are E or V is made. Having determined the triad structure (both comonomer and stereosequence) of the repeat unit selected for reduction, we divide the relative reactivity of this E–V triad by the sum of relative reactivities for all V-centered E-V triads as listed in Table II to obtain the probablity of reduction. A random number between 0.0 and 1.0 is generated, and if it is smaller than the probability of reduction of the selected E–V triad, we remove the chlorine from the central V unit, which becomes an E unit.

If either of the terminal units of the E–V triad selected are V units, then we modify their relative reactivities to reflect changing the central unit from V to E. The degree of reduction *x* is calculated from $100 \times$ (no. of chlorines removed ÷ 1000), and if it corresponds to the desired level of reduction, we print out the numbers of each type of triad remaining in the E–V copolymer. This whole procedure is repeated for several PVC chains until the fraction of each E–V triad type at each degree of reduction remains constant when averaged over the generated set of chains.

Figure 7 presents a comparison of observed and simulated E–V triad composition plotted against the degree of overall reduction by $(n\text{-Bu})_3$SnH. The agreement is excellent, being much improved over that found for TCH reduction. This is at least partially a consequence of the relative accuracy of the ^{13}C NMR data used to obtain the E–V triad compositions resulting from the reduction of PVC, because the TCH data are gathered during reduction and are an average over the time required to accumulate ^{13}C NMR spectra (~10 min), while E–V data are obtained on static samples removed from the reduction flask.

In Figure 8 we have plotted the ratios of *r*/*m* VV diads observed by ^{13}C NMR in E–V copolymers obtained by the

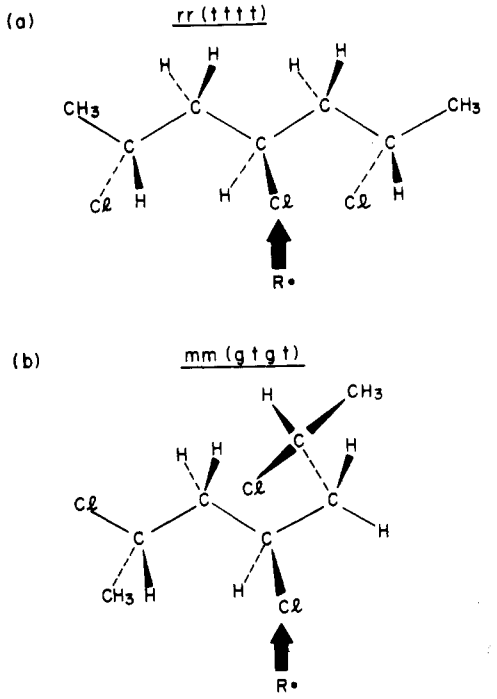

Figure 9. (a) *rr* and (b) *mm* isomers of TCH in the *tttt* and *gtgt* conformations.

$(n\text{-Bu})_3$SnH reduction of PVC[2]. They are compared to the *r*/*m* ratios resulting from our computer simulation of PVC reduction made possible by the observations of the kinetics of $(n\text{-Bu})_3$SnH reduction of DCP and TCH. The agreement is good and provides us with a knowledge of E–V stereosequence as a function of comonomer composition.

The excellent agreement between the simulated and observed reduction of PVC with $(n\text{-Bu})_3$SnH means that both DCP and TCH are appropriate model compounds for the study of PVC reduction. DCP is useful to obtain kinetic information on the relative reactivities of *m* and *r* diads and VV and EV diads. Reduction of TCH yields the relative reactivities of the central and terminal chlorines in the VVV triads.

With the $(n\text{-Bu})_3$SnH reduction of PVC successfully simulated via the kinetic studies of DCP and TCH reduction, it remains to explain the mechanisms[11] of this reductive dechlorination. We need only consider the mechanisms of the reduction of DCP and TCH, because we have demonstrated that the kinetics of their reduction are the same as those observed for PVC when also reduced by $(n\text{-Bu})_3$SnH.

Possible Mechanism for the Reduction of PVC with $(n\text{-Bu})_3$SnH. The reductions of alkyl halides with $(n\text{-Bu})_3$SnH are known[12] to be free radical chain reactions, where the $(n\text{-Bu})_3$Sn· radical (R·) abstracts the halogen (X) from the alkyl halide (R′X) creating an alkyl radical (R′·) and $(n\text{-Bu})_3$SnX. In Figure 9 the *rr* and *mm* isomers of TCH are depicted in their most probable conformations (*tttt* and *gtgt*),[13] with their central Cl's about to be abstracted by the R·. Attack at the central chlorine by R· is hindered[11] by both adjacent methine protons in the *tttt* conformer of *rr*-TCH, while only a single methine proton obstructs the radical attack of the central chlorine in the *gtgt* conformer of *mm*-TCH. We would expect, as is observed, the *mm* isomer to be more readily reduced than the *rr* isomer based solely on considerations of steric interactions.

Since the $(n\text{-Bu})_3$Sn· radical (R·) is nucleophilic,[14] a partial negative charge must be produced at the methine carbon whose chlorine is being abstracted. The rate of this abstraction should clearly be enhanced by electron-withdrawing groups on R′· due to their stabilization of this charge by inductive effects. As observed, the removal of Cl from EVV (or VV diad) is expected to be more facile than from EVE (or VE diad) as a result of a γ-halogen effect in the former structure.

Thus, the enhancements in chlorine removal from VV diads compared to EV diads and from *m*-VV diads compared to *r*-VV diads observed in the $(n\text{-Bu})_3$SnH reduction of DCP, TCH, and PVC are consistent with the free radical chain reaction mechanism. Inductive effects produced by neighboring γ-Cl's tend to favor the reduction of VV diads relative to EV diads, and steric interactions resulting from different preferred conformations in each isomer favor the removal of Cl from *m*-VV diads relative to *r*-VV diads.

Registry No. DCP, 625-67-2; TCH, 13049-21-3; PVC, 9002-86-2; Bu_3SnH, 688-73-3.

References and Notes

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