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Six-Center Concerted Mechanism for Poly(vinyl chloride) Dehydrochlorination. *Requiescat in Pace?*

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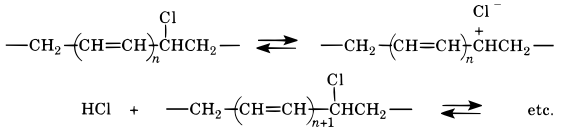
Poly(vinyl chloride) (PVC) has low intrinsic thermal stability because of its facile dehydrochlorination to form conjugated polyene sequences.[1] The effects of this process on polymer properties are acutely deleterious. Thus the mechanism of the reaction has been subjected to an enormous amount of basic research as well as speculation.[1] A contemporary appraisal[1a] has concluded, however, that the mechanism involves ion pairs (as in eq 1) or unsymmetrical four-center transition states with highly polarized C−Cl bonds.



$$-CH_2\!-\!(CH{=}CH)_n\!-\!\overset{Cl}{\overset{|}{C}}HCH_2- \rightleftarrows -CH_2\!-\!(CH{=}CH)_n\!-\!\overset{Cl^-}{\overset{+}{C}}HCH_2- \longrightarrow HCl + -CH_2\!-\!(CH{=}CH)_{n+1}\!-\!\overset{Cl}{\overset{|}{C}}HCH_2- \rightleftarrows \text{etc.} \qquad (1)$$

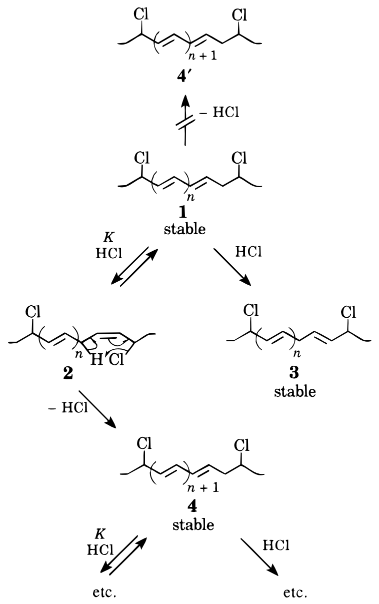
Very recently, the alternative mechanism shown in Scheme 1 has been advocated tenaciously by Bacaloglu and Fisch, who have reached the following conclusions.[2] The all-trans structure, **1**, in PVC is thermally stable at the temperatures where the polymer eliminates HCl. Thus, dehydrochlorination at the chloroallylic end of **1** (i.e., the **1** → **4′** conversion) does not occur at all. However, HCl catalysis readily rearranges **1** into **2**, which contains an isolated cis double bond. This structure dehydrochlorinates very rapidly to form **4** in a six-center concerted process (see arrows). The all-trans segment (**3**) produced together with **2** is inert like **1**, but the HCl-promoted conversion of **4** into a structural cognate of **2** allows polyene growth to continue.

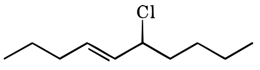
The mechanism of Scheme 1 predicts, therefore, that linear *trans*-homoallyl chlorides will dehydrochlorinate much more readily than linear *trans*-allyl chlorides. In contrast, the mechanism of eq 1 (or its four-center variant) predicts that the converse will be true, because the cations (or polarized transition states) formed from homoallyl chlorides will not be resonance-stabilized with respect to dispersion of positive charge.

Several detailed kinetic studies have been performed on dehydrochlorinations of allyl chlorides in the liquid phase.[1] Similar investigations of homoallyl chlorides seem to be lacking, but the threshold temperature for dehydrochlorination of liquid 4-chloro-1-hexene has been found to be 200 °C,[3] a value higher by 70 °C than that of the allyl chloride 3-chloro-1-pentene in the liquid phase.[3] These findings obviously augur ill for the mechanism of Scheme 1, but stronger kinetic evidence obtained from better models has been desirable.

When *n* in **1** is greater than 0, the **1** → **2** isomerization will be disfavored by a decrease in resonance energy of ca. 4 kcal/mol.[4] On the other hand, polyene growth should hasten HCl loss at the allyl chloride end of **1** by increasing the resonance stabilization of the incipient allylic cation.[4a,5] According to the results of MNDO calculations,[2e,g,i] when *n* in **2** goes from 0 to 1, six-center dehydrochlorination is not expedited and may even be slowed. Thus, for all of these reasons, the rate of the six-center process (**1** → **2** → **4**), relative to that of the **1** → **4′** transformation, should have its maximum value when only one double bond is present. With that conclusion in mind, we have used compounds **5** and **6** in order to compare the thermal stabilities of the ends of structure **1** when the value of *n* is 0.

Scheme 1. Proposed Six-Center Concerted Mechanism for the Thermal Dehydrochlorination of PVC[2]





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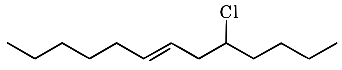
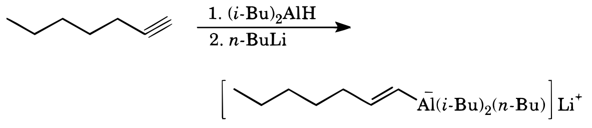


6

Allyl chloride **5** was made by the method reported previously,[6] which involves the regio- and stereospecific alkylation of *trans*-1-chloro-2-hexene with 1-bromobutane. The alkylation is carried out at −78 °C and requires introduction of the hindered strong base, $(i\text{-}Pr)_2NLi$.[7] In order to synthesize **6**, the sequence shown in eqs 2−4 was used. Here the preparation of alcohol **8** *via* **7** was adapted from published procedures[8] for the conversion of 1-alkynes into *β*-hydroxy-*trans*-alkenes. After distillation, the purities of **5** and **6** were ca. 95%, as determined from GC/MS and ^1H NMR data, which also showed that minor amounts of elimination products (dienes) were present in both materials. The IR spectra of **5** and **6** displayed a strong band near 965 cm^{-1}, as expected for trans geometry, and the structures of both chlorides were confirmed by ^1H and ^{13}C NMR measurements.[9]



(2)

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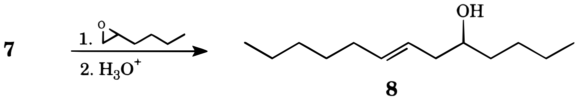

(3)

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$$\mathbf{8} \xrightarrow[DMF]{SOCl_2} \mathbf{6} \qquad (4)$$

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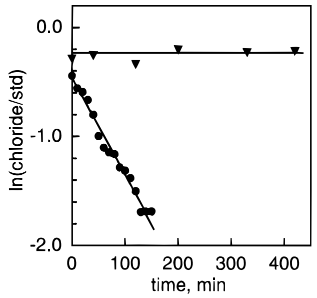

Figure 1. Kinetic plots for the thermal degradation of compounds **5** (●) and **6** (▼) in *o*-dichlorobenzene at 170 °C under argon. For details, see the text.

Degradation experiments with **5** and **6** were carried out under argon at 170 ± 2 °C in a Pyrex flask that was immersed in a thermostated oil bath. The flask was equipped with an efficient condenser, a side arm closed by a rubber septum (for sample withdrawal), and a bubbler that allowed the admission of a very slow stream of argon (ca. 0.7 mL/min) into reaction mixtures. The mixtures contained an internal standard (*n*-dodecane) and were analyzed periodically with a GC/MS apparatus containing a Hewlett-Packard Ultra 1 (cross-linked methylsilicone) column. Control runs showed that the model chlorides were stable under the conditions of the analyses.

In all degradation experiments with **5**, after only a few minutes of heating, the chromatographic peak for this substance began to separate into two components that were only partially resolved. These peaks were easily assigned to **5** and its rearranged isomer, *trans*-4-chloro-5-decene (**9**),[10] on the basis of an NMR study of a similar thermolysis.[11] Under our degradation conditions, the **5**/**9** mixtures were converted cleanly into mixtures of decadienes, which were identified from their mass spectra.

In order to determine first-order rate constants (k values) for dehydrochlorination,[1a] GC peak areas were used to obtain values of ln(chloride/standard)[12] that were plotted vs time. Values of k were then derived from the slopes of the straight lines thus obtained. First the two models were studied separately in *o*-dichlorobenzene solutions that were ca. 0.6 M in **5** or **6** and ca. 0.6 M in *n*-dodecane. Representative rate plots made for these runs are shown in Figure 1. In the case of **5** (actually, **5**/**9**), duplicate experiments gave an average k value of $9.1 \pm 0.3 \times 10^{-3}$ min^{-1}, which is well within a range of values found for **5** under similar degradation conditions.[1a] However, in striking contrast, as Figure 1 discloses, compound **6** did not degrade at an observable rate.

Since HCl catalysis was crucial in the mechanism of Scheme 1, mixtures of **5** and **6** were studied in order to ensure that both models were being subjected to the same concentration of HCl. In a typical degradation of this type, also performed in *o*-dichlorobenzene, equimolar amounts (0.34 M) of **5**, **6**, and the internal standard were used. In this case the k value found for **5** was 7.0×10^{-3} min^{-1}, but as before, no degradation of **6** was detected, even after a heating period of 24 h.

Finally, equimolar mixtures of **5**, **6**, and *n*-dodecane were degraded without solvent or agitation and under a static argon pressure, rather than with argon flow. These modifications were designed to maximize the HCl concentration in the liquid phase. They raised the rate constant for compound **5** up to 10.3×10^{-3} min^{-1} but brought about no reaction of **6** after 15 h of heating.

The experimental data allowed estimation of the maximum amounts of **6** that could have degraded without detection at various reaction times. These results were used to calculate the maximum possible values of k for **6**, which showed that under our conditions, **6** was more stable than compound **5** by a factor of 10^2–10^3, at least. This observation validates most strikingly our previously published arguments against six-center dehydrochlorination,[4a] one of which was that the equilibrium constant, K, for **1** $\rightleftarrows$ **2** interconversion is very small when n is greater than zero (from thermodynamic information, K was estimated[4a] to be ca. 3.5×10^{-4} at 170 °C). Bacaloglu and Fisch[2i] have asserted that the K value actually is much larger (in the range of 0.4–0.7), because the change from homoallyl to allyl chloride (considered apart from alterations in configuration and conjugation) is favored by a ΔG decrease of some 3.2–3.6 kcal/mol. The latter conclusion was based directly upon thermodynamic data which showed that, at 170 °C, 4-chloro-1-butene (**10**) is less stable, by 3.2–3.6 kcal/mol, than 3-chloro-1-butene (**11**) and 1-chloro-2-butene (**12**, presumably the trans isomer).[2i] However, values of ΔG_f° determined for other aliphatic alkenes and chlorides[13] reveal that the higher stabilities of **11** and **12** must result, to a large degree, from the primary-to-secondary C–Cl change upon going from **10** to **11** and the terminal-to-internal double-bond change upon going from **10** to **12**. Such structural transitions are not involved in the **1** $\rightleftarrows$ **2** interconversion. Thus the Bacaloglu–Fisch values of ΔG for that process are not correct, and their estimated values of K are much too high for that reason.

We conclude that the six-center concerted mechanism of Scheme 1 now has been shown not to operate during the thermolysis of PVC. The evidence for the ionic pathway (eq 1) or its quasiionic four-center alternative will be reviewed in detail elsewhere.[14]

Acknowledgment. We thank the National Science Foundation for support of this work under Grant No. DMR-9312048.

References and Notes

(1) (a) Starnes, W. H., Jr.; Girois, S. *Polym. Yearbook* **1995**, *12*, 105 (see also references cited therein). (b) Iván, B.; Kelen, T.; Tüdös, F. In *Degradation and Stabilization of Polymers*; Jellinek, H. H. G.; Kachi, H., Eds.; Elsevier: New York, 1989; Vol. 2, Chapter 8 (see also references cited therein).

(2) (a) Bacaloglu, R.; Fisch, M. *Polym. Degrad. Stab.* **1994**, *45*, 301. (b) Bacaloglu, R.; Fisch, M. *Polym. Degrad. Stab.* **1994**, *45*, 315. (c) Bacaloglu, R.; Fisch, M. *Polym. Degrad. Stab.* **1994**, *45*, 325. (d) Bacaloglu, R.; Fisch, M. *Polym. Degrad. Stab.* **1995**, *47*, 9. (e) Bacaloglu, R.; Fisch, M. *Polym. Degrad. Stab.* **1995**, *47*, 33. (f) Fisch, M.; Bacaloglu, R. *Annu. Tech. Conf.—Soc. Plast. Eng.* **1995**, 53rd(Vol. 3), 4166. (g) Bacaloglu, R.; Fisch, M. *Annu. Tech. Conf.—Soc. Plast. Eng.* **1995**, 53rd(Vol. 3), 4171. (h) Fisch, M. H.; Bacaloglu, R. *J. Vinyl Addit. Technol.* **1995**, *1*, 233. (i) Bacaloglu, R.; Fisch, M. H. *J. Vinyl Addit. Technol.* **1995**, *1*, 241.

(3) Suzuki, T.; Nakamura, M. *Jpn. Plast.* **1970**, *4* (2), 16.

(4) (a) Starnes, W. H., Jr. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1996**, *37* (1), 697. (b) Doering, W. von E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6037 (see also references cited therein).

(5) Haddon, R. C.; Starnes, W. H., Jr. *Adv. Chem. Ser.* **1978**, *No. 169*, 333.

(6) Haynie, S. L.; Villacorta, G. M.; Plitz, I. M.; Starnes, W. H., Jr. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1983**, *24* (2), 3.

(7) Macdonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504.

(8) (a) Warwel, S.; Schmitt, G.; Ahlfaenger, B. *Synthesis* **1975**, 632. (b) Negishi, E.; Baba, S.; King, A. O. *J. Chem. Soc., Chem. Commun.* **1976**, 17.

(9) Conditions: $CDCl_3$ solvent, ambient temperature, 300.52 MHz for ^{1}H, 75.57 MHz for ^{13}C, shifts vs internal Me_4Si at δ 0.00 ppm. Compound **5**: ^{1}H NMR δ 0.89 (t, 6H, $2CH_3$), 1.3−1.5 (m, 6H, $CH_2CH_2CH{=}$ and $CH_2CH_2CH_2CH_3$), 1.67−1.85 (d of t, 2H, CH_2CHCl), 2.01 (qrt, 2H, $CH_2CH{=}$), 4.32 (qrt, 1H, $CHCl$), and 5.4$_5$−5.7 ppm (m, 2H, $CH{=}CH$); ^{13}C NMR chemical shifts identical (±0.2 ppm) to those reported previously.[10] Compound **6**: ^{1}H NMR δ 0.8−1.1 (m, 6H, $2CH_3$), 1.2−1.4$_5$ (m, 10H, $CH_2CH_2CH_2CH_2CH{=}$ and CH_2CH_2-CH_2CHCl), 1.6−1.8 (m, 2H, $CHClCH_2$−*n*-Pr), 2.00 (qrt, 2H, CH_2-*n*-Bu), 2.42 (t, 2H, $={CHCH_2CHCl}$), 3.83 (qnt, 1H, $CHCl$), and 5.3−5.6 ppm (m, 2H, $CH{=}CH$); ^{13}C NMR δ 13.96 (C-13), 14.05 (C-1), 22.34 (C-12), 22.60 (C-2), 28.67 (C-11), 29.16 (C-4), 31.45 (C-3), 32.62 (C-5), 37.51 (C-10), 41.78 (C-8), 63.29 (C-9), 125.60 (C-7), and 134.19 ppm (C-6).

(10) Katz, H. E.; Starnes, W. H., Jr. *J. Org. Chem.* **1984**, *49*, 2758.

(11) Seshadri, S. R.; Starnes, W. H., Jr., unpublished observations of the thermolysis of *cis*-6-chloro-4-decene.[4a]

(12) Here “chloride” is the peak area of **6** or the **5**/**9** mixtures, and “standard” is the peak area of *n*-dodecane.

(13) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; Chapters 9 and 12.

(14) Starnes, W. H., Jr., in preparation for submission to *Polym. Degrad. Stab.*

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