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Mechanism of Elimination Reactions. 28. Stereochemistry of Elimination Reactions of 2- and 3-Hexyl Tosylates[1]

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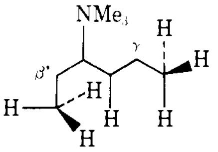
Abstract: The rate of reaction of 3-hexyl tosylate with *tert*-butoxide in *tert*-butyl alcohol depends on the cation in the order K > Na ≫ Li. The stereochemistry of elimination with 3-hexyl-*4-d* tosylate and sodium *tert*-butoxide in *tert*-butyl alcohol containing dimethyl sulfoxide runs (percent syn → trans, percent dimethyl sulfoxide) 28.4, 0; 19.9, 5; 9.3, 10; and 6.4, 90. Potassium *tert*-butoxide gives 20.3% syn → trans elimination. These results further confirm the favorable effect of base ion pairing on syn elimination from tosylates. 3-Hexyl-*4-d*, 3-hexyl-*2-d*, and 2-hexyl-*3-d* tosylates give 28.4, 16.6 and 12.3% syn → trans elimination, respectively. Examination of partial rates shows that the higher proportion of syn elimination from 3-hexyl-*4-d* tosylate arises essentially entirely from a decrease in the rate of the anti → trans path. These results are compared with those reported for structurally similar quaternary ammonium salts. While both can be explained by the steric theory of structural effects on the stereochemistry of elimination in acyclic systems, important questions remain.

Some time ago, we advanced a steric explanation[3,4] of the syn-anti dichotomy[5-8] (trans olefin partly or mainly by syn elimination, but cis olefin almost entirely by anti elimination) in E2 reactions of acyclic quaternary ammonium salts. According to this explanation, the bulky leaving group forced alkyl groups in the β' and γ positions (**1**) into a conformation



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such that they interfered with the approach of base to the anti-β hydrogen, and did so to a greater extent for the anti → trans than for the anti → cis path. A modification of this picture by Felkin, reported by Sicher,[9] allows for changes in dihedral angles due to steric congestion, but leaves the essential idea unchanged. The theory accounted very well for the effect of alkyl substitution at the β' and γ positions on the propensity for syn elimination.[4,10]

Subsequent reports made it clear, however, that the steric theory in its original form could not be correct. Alkyl fluorides, which have a much smaller leaving group than quaternary ammonium salts, nonetheless give major amounts of syn elimination.[11,12] In addition, partial rates of the various paths of elimination from acyclic quaternary ammonium salts show that the increase in syn elimination with increased steric requirements of the β' substituent arises mainly from increases in the rate of syn elimination, rather than the decreases in rate of anti elimination predicted by the steric theory.[13]

In order to gain further information on the effects of alkyl structure on stereochemistry of elimination in open-chain systems, we decided to examine the 2- and 3-hexyl systems[4] with a neutral leaving group of relatively modest steric requirements. While alkyl fluorides give substantial syn elimination, they react so sluggishly that some interconversion of the olefinic products occurs under the elimination conditions.[11,12] Consequently, we chose the tosylates, which give fairly small but significant amounts of syn elimination.[12,14,15]

Our first experiments used 3-hexyl-*4-d* tosylate and were aimed at finding conditions giving sufficient syn elimination that changes when the structure was changed would be readily observable. Prior evidence suggested that *tert*-butoxide[14,15] and strong ion pairing of the base with the metal ion[12] should be most favorable for syn elimination. The overall rate of reaction (Table I) was found to decrease sharply as the metal ion was changed from potassium to sodium to lithium, as expected for increasing ion pairing. In fact, the first two entries of Table I show that lithium *tert*-butoxide reacts so slowly that solvolysis constitutes a significant side reaction even at base concentrations as high as 1.0 M. Sodium *tert*-butoxide, however, gives <2% solvolysis at 0.5 M, and Table III shows that syn elimination accounts for nearly 30% of the *trans*-3-hexene. The smaller proportions of syn elimination with potassium *tert*-butoxide, and with sodium *tert*-butoxide in *tert*-butyl alcohol containing dimethyl sulfoxide, confirm the importance of ion pairing.

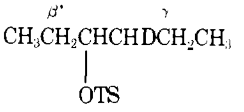
The erythro and threo stereoisomers of 3-hexyl-*4-d* (**2**), 3-hexyl-*2-d* (**3**), and 2-hexyl-*3-d* (**4**) tosylates were prepared as described in the Experimental Section and treated with sodium *tert*-butoxide in *tert*-butyl alcohol at 80 °C. The olefin proportions (Table II) and the deuterium analyses of the olefins (Table III) were combined as previously described[4] to give values for the percentages of syn elimination which would be observed in the absence of an isotope effect. The average values for percent syn → trans run **2**, 28.4; **3**, 16.6; and **4**, 12.3.

When the structures of **2–4** are written as shown, it becomes apparent that the most syn elimination is found when both the β' and γ positions contain alkyl substituents, while much less

Table I. Rate Constants and Proportions of Elimination and Substitution in Reactions of Hexyl Tosylates at 80 °C

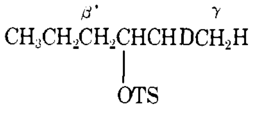
Reaction condn[a]	Reactant	$k_2 \times 10^6$, l mol^{-1} s^{-1}	Hexenes, %	Ether, %
t-BuOH	3-Hexyl	2.60[b]	*c*	*c*
t-BuOLi	3-Hexyl	41.1[d]	*c*	*c*
t-BuONa	3-Hexyl	323	91.2	8.8
t-BuOK	3-Hexyl	721	*c*	*c*
t-BuONa	2-Hexyl	772	88.0	12.0

[a] Base concentration 0.2–0.3 M, substrate concentration 0.1–0.2 M. Solvent is *tert*-butyl alcohol. [b] First-order rate constant (in reciprocal seconds) for solvolysis in the presence of 2,6-lutidine. [c] Not determined. [d] Not corrected for first-order component.



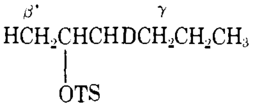
$\mathrm{CH_3\overset{\beta'}{C}H_2\underset{\underset{OTS}{|}}{C}HCHD\overset{\gamma}{C}H_2CH_3}$

2



$\mathrm{CH_3CH_2\overset{\beta'}{C}H_2\underset{\underset{OTS}{|}}{C}HCHD\overset{\gamma}{C}H_2H}$

3



$\mathrm{H\overset{\beta'}{C}H_2\underset{\underset{OTS}{|}}{C}HCHD\overset{\gamma}{C}H_2CH_2CH_3}$

4

is observed when only the β′ position is alkyl substituted, and somewhat less again when only the γ position is alkyl substituted. This is qualitatively the same order as found for the corresponding quaternary ammonium salts,[4] although in that case the larger decrease was between the last two rather than the first two members of the series.

In order to determine whether the causes of this order are the same for the tosylates and the quaternary ammonium salts, we combined the rate data (Table I) with product analyses (Tables II and IV), and proportions of syn elimination (Table III) to get partial rates for the formation of each olefinic product by syn and anti paths. The results are given in Table IV. While the combination of these different pieces of data certainly magnifies error, the figures are probably good to 10–20%.

Table IV shows clearly that the rate of the syn → trans path is little affected by changes in the substitution pattern at the β′ and γ positions, and that the greater proportion of syn elimination from **2** than from **3** or **4** arises essentially entirely from a sharp (ca. threefold) decrease in the rate of the anti → trans path for **2**. A similar, but less sharp, decrease is noted for the anti → cis path. In both cases, the significant difference in rate is between **2** and the other two; substituents at *both* the β′ and γ positions are necessary to bring about the rate decrease.

Comparison of our results with those of Pânková and Závada[13] on the quaternary ammonium salts in Table V reveals marked differences. While the same compounds were not used in the two studies, the trends are clear. Replacement of hydrogen by alkyl at the β′ position causes a dramatic increase in the syn → trans path with the quaternary ammonium salts, but no significant change with the tosylates (entries 4 and 5 vs. entries 1 and 3). The same data show an increase in the anti → trans rate for the quaternary ammonium salts and a decrease for the tosylates with β′ substitution. On the other hand, the effects of alkyl substitution at the γ position are similar for the quaternary ammonium salts and the tosylates: slight decreases in the syn → trans, and marked decreases in the anti → trans and anti → cis rates (entries 2 and 3 vs. entries 7 and 8). Extension of the alkyl substitution from methyl to ethyl (entries 5 and 6, and 8 and 9) has little effect on any of the partial rates and supports the validity of comparisons between

Table II. Product Proportions from Elimination Reactions of the Hexyl Tosylates at 80 °C

Reaction condn[a]	Reactant[b]	Hexenes, %[c,d] *trans*-**3**	*cis*-**3**	*trans*-**2**	*cis*-**2**
	A. For 3-Hexyl-*4-d* Tosylate				
t-BuOK	H	11.3	19.5	22.2	47.0
	erythro-4-d	4.3	18.9	22.6	54.2
	threo-4-d	8.3	9.9	23.9	57.9
t-BuONa	H	7.6	21.8	17.2	53.4
	erythro-4-d	4.9	21.2	19.9	54.0
	threo-4-d	8.9	10.4	21.3	59.4
	erythro-2-d	9.9	23.2	9.6	57.3
	threo-2-d	11.9	30.9	23.8	33.4
t-BuONa, 5% Me$_2$SO	H	11.4	17.2	27.2	44.2
	erythro-4-d	6.3	17.5	27.7	48.5
	threo-4-d	11.4	8.2	29.6	50.8
t-BuONa, 10% Me$_2$SO	H	16.8	13.2	33.7	36.3
	erythro-4-d	9.8	14.7	37.4	38.1
	threo-4-d	17.8	6.6	37.5	38.1
t-BuONa, 90% Me$_2$SO	H	26.7	7.1	48.0	18.2
	erythro-4-d	10.7	8.4	58.5	22.4
	threo-4-d	26.3	3.1	50.2	20.4
	B. For 3-Hexyl-*2-d* Tosylate				
t-BuONa	H	7.6	21.8	17.2	53.4
	erythro-2-d	9.9	23.2	9.6	57.3
	threo-2-d	11.9	33.6	23.7	30.8
	C. For 2-Hexyl-*3-d* Tosylate				
t-BuONa	H			8.3	19.3
	erythro-3-d			4.3	18.8
	threo-3-d			6.2	10.5

[a] Base concentration 0.45–0.50 M; substrate concentration 0.05–0.06 M. Solvent is the conjugate acid of the base, except where the indicated percentage is replaced by Me$_2$SO (dimethyl sulfoxide). [b] H refers to undeuterated reactant. The *erythro-4-d* contains 4.2% undeuterated material; *threo-4-d*, 1.9%; *erythro-2-d*, 6.9%; *threo-2-d*, 2.5%; *erythro-3-d*, 2.7%; *threo-3-d*, 2.8%. [c] See Experimental Section for conditions of analysis. [d] Corrected for olefin from undeuterated material (see footnote *b*) in deuterated reactants.

Table III. Deuterium Analyses of Hexenes and Stereochemistry of Elimination from Deuterated Hexyl Tosylates at 80 °C

Reaction condn[a]	Reactant[b]	Olefin fraction[c]	d_0, % obsd	% syn[d] Uncorr	% syn[d] Corr
	A. For 3-Hexyl Tosylates				
t-BuOK	*erythro-4-d*	*t*	12.6	45.1	21.5
	threo-4-d	*t*	4.4	9.7	19.1
					av 20.3
	erythro-4-d	*c*	4.5	(1.2)	(2.5)[e]
	threo-4-d	*c*	15.4	(7.1)	(2.5)[e]
t-BuONa	*erythro-4-d*	*t*	12.7	57.0	30.6
	threo-4-d	*t*	6.0	13.9	26.2
					av 28.4
	erythro-4-d	*c*	4.5	(1.2)	(2.5)[e]
	threo-4-d	*c*	16.5	(7.1)	(2.5)[e]
t-BuONa, 5% Me_2SO	*erythro-4-d*	*t*	14.7	43.3	20.3
	threo-4-d	*t*	4.5	9.4	18.5
					av 19.9
t-BuONa, 10% Me_2SO	*erythro-4-d*	*t*	19.4	26.7	10.8
	threo-4-d	*t*	3.1	3.7	7.8
					av 9.3
t-BuONa, 90% Me_2SO	*erythro-4-d*	*t*	17.1	16.9	6.4
	threo-4-d	*t*	2.9	2.9	6.4
					av 6.4
t-BuONa	*erythro-2-d*	*t*	37.5	37.9	16.9
	threo-2-d	*t*	7.8	8.1	16.3
					av 16.6
	erythro-2-d	*c*	7.7	(1.2)	(2.5)[e]
	threo-2-d	*c*	45.8	(14.9)	(5.5)[e]
	B. For 2-Hexyl Tosylates				
t-BuONa	*erythro-3-d*	*t*	6.3	30.1	12.5
	threo-3-d	*t*	3.2	5.9	12.1
					av 12.3

[a,b] See corresponding footnotes in Table II. [c] *t* refers to *trans*-2- + *trans*-3-hexene, *c* to *cis*-2- + *cis*-3-hexene. [d] The uncorrected value is calculated by comparing d_0, % obsd, with that calculated for syn and anti elimination, using data in Table II. The corrected value is corrected for assumed isotope effects of $(k_H/k_D)_{anti} = 3.0$ and $(k_H/k_D)_{syn} = 2.2$. See ref 4. [e] The corrected % syn values are assumed, and then used to calculate % d_0 for the starting material (see footnote *b*, Table II, for the resulting values). The uncorrected values are simply those values which give the corrected values after the corrections for isotope effects (footnote *d*). See the Experimental Section for further details.

Table IV. Partial Rates for Elimination from Hexyl Tosylates with Sodium *tert*-Butoxide in *tert*-Butyl Alcohol at 80 °C

Reactant	Product	$k_2 \times 10^5$, mol^{-1} s^{-1} for[a] syn	Anti	Total
3-Hexyl	*trans*-3-Ene	0.64	1.60	2.24
	cis-3-Ene	0.2[b]	6.22	6.42
	trans-2-Ene	0.84	4.23	5.07
	cis-2-Ene	0.4[b]	15.3	15.7
	Ether			2.84
2-Hexyl	*trans*-2-Ene	0.69	4.95	5.64
	cis-2-Ene	0.3[b]	12.8	13.1
	1-Ene			49.2
	Ether			9.26

[a] The column headed "total" is obtained by multiplying the titrimetric second-order rate constant (Table I) by the fraction of the specified product (Tables I and II). It is broken down, where appropriate, into syn and anti contributions using the average fractions (from threo and erythro reactants) of syn and anti elimination corrected for the deuterium isotope effects (Table III). [b] These values are based on an assumed 2.5% syn → cis reaction (see Table III and the Experimental Section), and are reliable only as orders of magnitude.

Table V. Partial Rates for Eliminations from *sec*-Alkyl Tosylates and Trimethylammonium Salts with *tert*-Butoxide in *tert*-Butyl Alcohol[a]

Leaving group	$R_{\beta'}$	R_γ	$k_2 \times 10^5$ l mol^{-1} s^{-1} for s → t[b]	a → t[b]	a → c[b]
OTs	H	Et	0.69	4.95	12.8
	Et	H	0.84	4.23	15.3
	Me	Me	0.64	1.60	6.22
NMe_3^+	H	Bu	0.012	0.069	0.32
	Me	Bu	0.66	0.14	0.27
	Et	Bu	0.75	0.092	0.25
	Bu	H	0.97	0.43	1.98
	Bu	Me	0.76	0.16	0.29
	Bu	Et	0.86	0.11	0.36

[a] Figures for the tosylates are from data in Table IV. Data for the quaternary ammonium salts with potassium *tert*-butoxide in *tert*-butyl alcohol are from ref 13. [b] s, syn; t, trans; a, anti; c, cis.

results on the tosylates and the longer chain quaternary ammonium salts.

The partial rates for the tosylates are in good agreement with the steric theory of syn elimination in open-chain systems.[4] The anti → trans and anti → cis processes are slowed by β' and γ substitution, but the former more so. Furthermore, substitution at both the β' and γ positions is required to hinder anti elimination significantly. This sort of cooperative effect is just what one would expect from a conformation such as **1**, where the β' and γ substituents effectively enclose the anti-β hydrogen. The absence of either would leave the hydrogen open to attack on one side.

If the steric explanation is correct, it is evident that a bulky leaving group is not necessary to favor conformation **1** for the elimination transition state. One plausible factor would be repulsion between the hydrocarbon-like ends of the alkyl chains and the leaving group with its partial charge (negative for the tosylate and positive for the quaternary ammonium salt).

Another possibility would be the tendency of the hydrocarbon-like chain to coil up so as to present minimum surface area to the polar solvent.

Eventually one must face the paradox that the steric theory rather unexpectedly fits the tosylates, but does not fit the quaternary ammonium salts for which it would seem a priori more likely. Pánková and Závada[13] make the argument that ground-state steric strain may be greater in the longer chain quaternary ammonium salts and that it approximately cancels the steric hindrance to proton abstraction in the transition state, leading to little or no net effect on the rate of anti elimination. If there is substantially less hindrance to proton abstraction in the syn transition state, the net result would be a decrease in activation energy with increasing substitution, and the observed increase in rate. The tosylates, lacking the ground-state strain, follow the steric theory predictions in a more straightforward manner.

While one feels a natural reluctance to lend too much credence to the sort of fortuitous cancellation of effects postulated for the quaternary ammonium salts, it is hard to see how the effects involved could be anything but steric. Neither the β' nor γ substituent is directly attached to the developing double bond, and the intervening saturated carbon atom in each case should make any electronic effects quite weak. Evidence against a controlling polar effect has been presented for the related thermal decomposition of alkyldimethylamine oxides.[16] Here a sharp increase in rate with increasing β' substitution is observed, just as for the quaternary ammonium salts, but an *opposite* electronic effect (acceleration by electron-withdrawing meta and para substituents) is observed with 1-arylbutyldimethylamine oxides.

The steric theory of syn elimination, even as modified, is not without loose ends and uncertainties. For example, γ substitution decreases the rate of anti → cis elimination even more sharply, and anti → trans elimination just as sharply for the quaternary ammonium salts as for the tosylates, though the postulated ground-state strain would be expected to counteract the rate decrease to some degree with the quaternary ammonium salts. Furthermore, significant additions to steric *strain* in the ground state from β' and γ substitution do not seem too likely, as the substituents should be able to rotate so as to avoid serious nonbonding interactions with the trimethylammonio group. Perhaps the effect actually involves steric hindrance to solvation of the positive charge on the nitrogen, which should be more difficult to approach the longer the alkyl chain. Since the transition states for elimination from the quaternary ammonium salts with a negative base are overall neutral, solvation and hence hindrance to it should play a much smaller role. This should be particularly true of the syn elimination transition state, which has less charge separation than the anti elimination transition state.

Experimental Section[17]

threo-**3-Hexanol-*4-d*** was prepared in 67% yield, bp 134–135 °C, from *trans*-3-hexene, sodium borodeuteride, and boron trifluoride etherate, followed by oxidation of the resulting borane with alkaline hydrogen peroxide according to the procedure of Brown and Zweifel.[18]

erythro-**3-Hexanol-*4-d*** was prepared in 31% yield, bp 134–135 °C, from *cis*-3-hexene by the same procedure.

erythro-**3-Hexanol-*2-d*** and *erythro*-**2-hexanol-*3-d*** were prepared by the same procedure from *cis*-2-hexene. The mixture was separated by GLC on a 26 ft × 0.25 in. column of 15% diglycerol on 60/70 mesh ABS. The separated hexanols were shown by GLC analysis on the same column to be >98.5% pure.

threo-**3-Hexanol-*2-d*** and *threo*-**2-hexanol-*3-d*** were prepared from *trans*-2-hexene and separated in the same manner as above.

3-Hexyl *p*-toluenesulfonate was prepared in 70% yield by the method of Tipson,[19] recrystallized from petroleum ether at dry ice temperature, and dried in vacuo. Both the undeuterated and the various deuterated products had mp 25–26 °C (lit.[12] 25.5–26.5 °C).

2-Hexyl *p*-toluenesulfonate and the corresponding deuterated materials were prepared as above and purified on an alumina column using pentane as eluent. Removal of the pentane left a colorless liquid.

Base solutions were prepared as described by Borchardt and Saunders.[20]

Elimination reactions were carried out in stainless steel tubes[21] in a constant-temperature bath, using solutions 0.06–0.08 M in hexyl *p*-toluenesulfonate and 0.4–0.5 M in base. The cooled reaction mixture was subjected to short-path distillation into a receiver cooled by dry ice–acetone. Water was added to the distillate and the mixture extracted with pentane. When dimethyl sulfoxide was present, water was added directly to the reaction mixture followed by extraction with pentane.

Elimination Product Separation and Analysis. The four isomeric olefins from 3-hexyl *p*-toluenesulfonate were analyzed by GLC according to the procedure of Bailey and Saunders[4] using a Perkin-Elmer Model 900 gas chromatograph with flame ionization detectors. Separation of the olefins for mass spectrometric analysis was performed on a Varian Model 920 gas chromatograph according to the procedure of Borchardt and Saunders.[20]

Mass spectrometric analyses were performed on an Atlas MAT CH-4 mass spectrometer according to the procedure of Borchardt and Saunders.[20] Difficulty was encountered in determining the deuterium content of the starting materials because the hexanols gave complex mass spectra with no significant parent peaks. With the 2-hexyl-*3-d* tosylates, the 1-hexene was separated from the 2-hexenes by GLC, and its deuterium content was assumed to be the same as that of the starting material. For the 3-hexyl-*4-d* and 3-hexyl-*2-d* tosylates, estimates of the deuterium content were obtained from the deuterium contents of the *cis*-3- + *cis*-2-hexene fraction as follows. The fraction of syn → cis elimination was assumed to be 2.5%, and the d_0 content of starting material necessary to give this assumed value was calculated. The precise value assumed has little effect on the percent syn → trans values calculated from data on reactions of the erythro substrates; varying the assumed percent syn → cis value in the range 0–5% did not change percent syn → trans by more than experimental error. The percent syn → trans values from data on reactions of the threo substrates are much more sensitive to the assumed percent syn → cis, but the reasonable agreement of percent syn → trans values from the threo and erythro substrates (Table III) shows that the assumed value is reasonable, with one exception. A negative percent d_0 value results when 2.5% syn → cis is assumed for the reaction of *threo*-3-hexyl-*2-d* tosylate with sodium *tert*-butoxide. If 5.5% syn → cis is assumed in this case, a reasonable value of 2.5% d_0 results, and the percent syn → trans values from the threo and erythreo substrates are in good agreement. The assumed percent syn → cis values are reasonable by comparison with literature values, for 3-hexyl-*4-d* trimethylammonium salts[20] give 2–6%, and 5-decyl-*6-d* tosylates[14,15] 2–5% syn → cis elimination.

Calculations of the percentages of syn elimination for the parent undeuterated compounds followed the method of Bailey and Saunders,[4] assuming $(k_H/k_D)_{anti} = 3.0$ and $(k_H/k_D)_{syn} = 2.2$ in all cases. The arguments for these assumptions have been discussed previously.

Kinetic Procedure. For the E2 reactions, 25 mL of solution 0.1–0.2 M in hexyl tosylate and 0.2–0.3 M in base in a 100-mL volumetric flask capped with a septum was placed in a constant-temperature bath at 80 °C. At appropriate intervals, 2-mL samples were withdrawn by syringe, quenched in distilled water, and titrated with standard hydrochloric acid to the bromcresol green end point. The rate constant was calculated from the usual integrated second-order equation for unequal initial concentrations. The E1 reactions were carried out in the same way, but with 0.2 M 2,6-lutidine instead of alkoxide to prevent acid-catalyzed side reactions.[22] The rate constant was calculated from the usual integrated first-order equation.

Control Experiments. The isomeric hexenes were shown to be stable to the reaction conditions. The pentane used was shown to contain nothing which could interfere with the GLC or mass spectrometric analyses. The short-path distillation of the pentane solution of the hexenes was shown to have no effect on product proportions.

References and Notes

(1) This work was supported by the National Science Foundation.

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An Examination of the Thermal Polymerization of a Crystalline Diacetylene Using Diffuse Reflectance Spectroscopy

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Received April 18, 1977

Abstract: Diffuse reflectance spectroscopy is used to investigate the thermal polymerization of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS. Polymerization proceeds via a solid-state 1,4-addition to form a fully conjugated polymer chain. The polymerization rate is determined on a relative basis by monitoring the evolution of the optical band system which is characteristic of the PTS polymer. The temperature dependence of the polymerization rate, in the limit of low polymer conversion, is quite accurately described by an Arrhenius expression over the temperature range of the experiments reported here, 35–80 °C, which yields a 200-fold change in rate. The activation energy in this low conversion range is 21.9 ± 0.6 kcal/mol, which is about the same as that estimated at high conversions using polymer extraction techniques. At low conversions, the polymerization rate is constant at constant temperature. However, at higher conversions, an "autocatalytic" effect is observed as a tenfold increase in polymerization rate. This result is shown to require at least a tenfold increase in chain propagation length in the autocatalytic region.

Though diacetylenes have been known to polymerize for some time, the current interest in the polydiacetylenes stems largely from the recent work of Wegner, who identified the polymerization as a solid-state, 1,4-addition reaction.[1,2] In a number of instances this polymerization process has been shown to result in high perfection, large dimension polymer crystals.[3,4] The backbone is fully conjugated with two mesomeric representations, acetylene ($=RC-C\equiv C-CR=$) and butatriene ($-RC=C=C=CR-$), both of which have now been observed.[5-8] The polymer crystals are fully chain aligned and are effectively one dimensional in their optical properties.

The polymer of 2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate), PTS (R is $-CH_2SO_3C_6H_4CH_3$), exists as the acetylenic structure[5] and is now described in a rather extensive literature concerned with optical properties,[9-13] photoconduction,[14-16] and the polymerization process.[2,4,17,18] The polymerization process is particularly interesting in PTS because of the "autocatalytic" effect first reported by Wegner[2] and since reexamined by Bloor et al.[17] In both cases, an extraction procedure was used in which the weight fraction of insoluble polymer was determined as a function of exposure time at a particular temperature (60, 70, and 80 °C in the experiments of Bloor et al.[17]). After ~10% conversion to polymer, conversion vs. time curves show a rapid—almost discontinuous—rise to nearly 100% conversion to polymer. From these data, one can estimate that the polymerization rate increases by a factor of 100 or more in this autocatalytic region,[2,17] i.e., $\gamma_{max}/\gamma \gtrsim 100$ where γ is the polymerization rate in the low conversion limit. A reliable determination of γ_{max}/γ is quite important if a successful theoretical model for the autocatalytic effect is to be developed. The estimate from the extraction experiments cannot be considered very reliable because of a number of problems inherent in the extraction technique. First, the published data simply lack the accuracy that would be required for a reliable estimate. Also, a detailed study of the autocatalytic region is inhibited by the tedium of the extraction procedure. Finally, at low conversions where the crystals collapse on extraction, an unknown amount of polymer is lost by dissolving in the solvent (as we will discuss later) and by simply passing through the filter. At high conversions where the crystal integrity is maintained an unknown amount of monomer can be trapped in the lattice. (Intense grinding of the polymer with multiple extractions will eliminate this problem to some extent.)[17] Both of these problems would lead to overestimates of γ_{max}/γ, even if the accuracy of the data were improved. In this paper, we examine the thermal polymerization of PTS using diffuse reflectance spectroscopy and establish at least a firm lower limit for γ_{max}/γ. In addition, we accurately determine the activation energy for thermal polymerization of PTS and discuss the evolution of the spectra during polymerization.

The application of diffuse reflectance spectroscopy is now commonplace,[19] particularly in inorganic chemistry where it can be used, for example, to eliminate effects of solvent on the coordination sphere of metal ions.[20] For organic materials, solvent effects are usually more subtle and applications of