TABLE II: Initial Parameters for the Three Trajectories Shown in Figure 1

trajectory a	$f_{x} = 0.347$	$E_{\rm HH} = 4.331$	$E_{\rm HO} = 0.669$
trajectory b	$f_{x} = 0.650$	$E_{\rm HH} = 7.000$	$E_{\rm HO} = 3.000$
trajectory c	$f_{x} = 0.347$	$E_{\rm HH} = 12.50$	$E_{\rm HO} = 2.500$

The initial conditions for the Henon-Heiles portion of eq 7 are the same as given in Table II. The harmonic oscillator portion of eq 7 has energies, $E_{\rm HO}$, as given in Table II for trajectories a-c. For the reduced dimensionality plots only the harmonic oscillator coordinate (q_3) need be calculated. It is given by

$$q_3 = (2E_{\rm HO})^{1/2} \cos t \tag{8}$$

These reduced dimensionality plots for the three trajectories are shown in Figure 5. These lines should have theoretical slopes of 3 for the two totally quasiperiodic trajectories and 4 for the mixed stochastic-quasiperiodic trajectory. The least-squares slopes for these data are 3.05, 2.98, and 3.82, respectively.

III. Discussion and Summary

We have presented a numerical method to determine the number of constants of the motion for Hamiltonian systems. The method has been demonstrated for systems with two and three degrees of freedom but can, in principle, be easily extended to systems with larger numbers of degrees of freedom.

The method determines the number of degrees of freedom from the dimensionality of the surface in phase space on which the trajectory moves. This number is determined from the slope of the line produced in a dimensionality plot. Because this is a numerical procedure, some consideration has to be given to the bin size and to the number of time steps needed to establish convergence of the number of unique bins through which the trajectory travels. If the number of bins is large, then the trajectory will not have the opportunity to access all of the bins that may be available. Because the trajectory has a dimensionality of unity, a slope of unity for the line in a dimensionality plot would result if an insufficient number of time steps were generated. On the other hand, if the number of bins per direction were too small, then all the bins in phase space could be accessed and any trajectory would appear to be ergodic. These are extreme cases, and in fact a considerable range of bin sizes are available such that a valid slope in the dimensionality plot can be obtained.

We have assumed here that the dimensionality plot should yield an integer value for k, i.e., the Euclidean or topological dimensionality. Indeed, within the error limits of the calculations, the least-squares slopes agree with the theoretical values. It is known, however, that noninteger values for dimensionalities are possible for various physical systems. Examples are given in the theory of "fractals" as discussed in the very readable book by Mandelbrot.¹¹ In fact, the value of 2n - k calculated here represents the Hausdorff-Besicovitch dimensionality. If the trajectory travels on a multidimensional surface that is not "wellbehaved", the dimensionality of this surface (2n - k) would not necessarily be an integer but would be greater than the topological dimension.

Certain mappings exist for which fractional dimensionalities are indeed the case. However, for dynamical systems, because of their complexity, no such results can be proven. It is known that intricate phase-space structures occur in simple model Hamiltonians and indeed these structures may lead to noninteger dimensionalities.

We are extending this method by applying it to realistic triatomic systems.

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Stereochemistry of the Four-Centered Gas-Phase Dehydrohalogenation Reaction

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The stereochemistry of the gas-phase four-centered dehydrohalogenation reaction has been determined. Deuterium analysis of the 2-butene isomers formed by the thermal decomposition of threo- and erythro-2bromo-3-deuteriobutane proves that elimination is principally via a syn transition state; i.e., the hydrogen and halogen are removed from the same side of the carbon-carbon bond. The results show that the contribution of anti stereochemical transition state complexes is small, perhaps zero. Primary and secondary deuterium kinetic isotope effects were 2.11 \pm 0.31 and 0.98 \pm 0.12 respectively for erythro-2-bromo-3-deuteriobutane, and 2.07 ± 0.24 and 1.02 ± 0.13 respectively for three-2-brome-3-deuteriobutane at 590 K.

Introduction

One of the prototype gas-phase unimolecular processes is the α,β -dehydrohalogenation reaction.¹⁻³ Recent interest has centered on energy disposal,³⁻⁷ laser activation by absorption of multiple infrared photons,⁶⁻⁸ surprisal analysis of the hydrogen halide vibrational state distribution,⁵ and the molecular reorganizations at the transition state.^{3,9-11} In solution the nature of the transition state

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has been extensively studied. Usually the base-promoted process proceeds by an anti stereochemical pathway although the properties of the solvent, base, and halogen influence the mechanism.^{12,13} In the gas phase the elegant work of Barton and co-workers¹⁴ on the pyrolysis of (-)menthyl chloride established that syn elimination does occur. However, since the anti channel is blocked in (-)-menthyl chloride the presence of a competitive anti pathway could not be tested. Pyrolyses of neomenthyl chloride¹⁵ suggested concurrent anti elimination of HCl since 15% of the alkene products were 3-menthene. Direct formation of 3-menthene from neomenthyl chloride can only occur via an anti process. These results imply simultaneous anti and syn eliminations. In fact, Woodward-Hoffman rules^{16,17} predict an anti mechanism for a concerted [2a + 2a] pericylic reaction, whereas an ab initio molecular orbital calculation⁹ and the orbital phase continuity principle¹⁸ favor the syn process.

The goal of the present work is to determine by experiment the contribution of syn and anti transition states to the gas-phase dehydrohalogenation reaction. Our methodology was based on that of Skell and Allen,¹⁹ and Bartsch.²⁰ Thermal decomposition of d, l-three- or d, lerythro-2-bromo-3-deuteriobutane yields 1-butene, cis-2butene, and trans-2-butene. Analysis of the deuterium content of cis-2- or trans-2-butene produced from either of the two bromobutane diastereomers was used to elucidate the stereochemistry of the transition state. Assuming only syn elimination occurs, the following scheme illustrates the deuterium location.

$$\begin{array}{ccc} \text{Br} & \xrightarrow{\text{syn}} trans-2\text{-butene-}d_0 + \text{DBr} & (1a) \\ & & & & & \\ & & & & & \\ & & & & & \\ \end{array}$$

$$CH_3 \rightarrow cis-2$$
-butene- $d_1 + HBr$ (1b)

$$\xrightarrow{\text{opt}} 1 \text{-butene-} d_1 + \text{HBr} \qquad (1c)$$

2 ervthro

Br
$$\xrightarrow{\text{syn}}$$
 trans-2-butene- d_1 + HBr (2a)

$$\mathbf{C}_{\mathsf{H}_{\mathbf{3}}} \xrightarrow{\operatorname{cis-2-butene-}d_{\mathfrak{0}}} + \mathsf{DBr}$$
(2b)

$$\xrightarrow{201}$$
 1-butene- d_1 + HBr (2c)

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Identical olefin deuterium substitution would be observed for HBr (DBr) elimination from either member of the d.lpair of either erythro- or threo-2-bromo-3-deuteriobutane, therefore, only one of the optical isomers is shown in reactions 1 and 2 and the optical isomer designation will be neglected. For anti elimination the location of the deuterium would be reversed between the cis-trans isomers of 2-butene. Thus, mass analysis of the cis-2-butene or trans-2-butene product from either erythro or three will define the stereochemistry in the transition state complex, provided that cis-trans isomerization is negligible.

A critical requirement for this work is that interconversion of the three butene isomers be arrested or sufficiently small so that correction can be made for the isomerization. In the absence of inhibitors, the surface of the pyrolysis vessel and HBr are effective catalysts^{2,21-23} of the butene isomerization reaction. Proper treatment of the reactor quenches the surface-initiated reactions.²¹ Catalysis by HBr is not as readily suppressed, therefore, *cis*-2-butene or trans-2-butene was pyrolyzed in the presence of hydrogen bromide and different amounts of cyclohexene, an efficient inhibitor,^{24,25} to ascertain the onset of maximum inhibition and the percentage isomerization remaining under those conditions.

Preparation of threo-2-bromo-3-deuteriobutane produced small quantities of bromobutane and erythro impurities. Similarly, synthesis of erythro gave small amounts of three and bromobutane.^{19,20,26} Since the fraction of each impurity must be known, the threo-rich and erythro-rich bromobutane samples were dehydrobrominated in solution. The percentage yield of each butene and its extent of deuteration was used to determine the percent purity of the threo-rich and erythro-rich samples.^{19,20,26}

The crucial set of experiments was the gas-phase pyrolysis of threo- or erythro-2-bromo-3-deuteriobutane in the presence of cyclohexene. The cyclohexene concentration was adjusted to achieve maximum inhibition of the hydrogen bromide catalyzed isomerization reaction. Analysis of the butene deuterium content for each isomer determined the stereochemistry of the α,β -elimination process. The butene percentage yields were measured for pyrolysis of threo-, erythro-, and 2-bromobutane- d_0 . Since the rate of 1-butene formation should be nearly identical for the three bromobutanes, the primary and secondary β -deuterium isotope effects were calculated from the butene percentage yields.

In spite of the problems associated with the olefin isomerization reactions the selection of threo- and erythro-2-bromo-3-deuteriobutane was based on four advantages relative to a chloro- or fluorobutane. (1) The HBr elimination activation energy is low relative to HCl and HF. Pyrolysis temperatures in the 570-620 K range²⁷⁻²⁹ can be employed where thermally induced cis-trans isomerization of 2-butene is neglible.²¹ (2) The threo- and erythro-2bromobutanes can be synthesized with a high degree of

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TABLE I: Experimental Percentage Yield and Percentage Deuterium Content of 1-Butene, *cis*-2-Butene, and *trans*-2-Butene from Solvolysis^a of Bromobutane and *threo*- and *erythro*-2-Bromo-3-deuteriobutane

bromobutane isomer	1-butene		trans-2-butene		cis-2-butene	
	% yield ^b	% deuteration ^c	% yield ^b	% deuteration ^c	% yield ^b	% deuteration ^c
undeuterated threo ^e erythro ^f	$21.2 \pm 1.2^{d} 24.5 \pm 0.9 35.7 \pm 1.3$	95.21 ± 0.37 95.85 ± 0.44	57.9 ± 1.4 66.0 ± 0.6 31.6 ± 0.8	94.96 ± 0.65 5.56 ± 0.69	$20.9 \pm 1.5 \\ 9.5 \pm 1.0 \\ 32.7 \pm 1.0$	18.6 ± 0.8 95.98 ± 0.52

^a 1.0 M KOEt in EtOH at 340 K for 90 min. ^b Average of 5-10 GLC traces. ^c Average of 10 (usually) MS traces. ^d One standard deviation. ^e Sample rich in *threo*-2-bromo-3-deuteriobutane; see text for actual composition. ^f Sample rich in *erythro*-2-bromo-3-deuteriobutane; see text for actual composition.

stereospecificity.^{19,26} (3) Many haloalkane compounds thermally decompose via a radical chain mechanism. For bromobutane the molecular mechanism is dominant.²⁷⁻²⁹ (4) Thermally induced addition of HBr to the butenes, the reverse of the elimination reaction, is not important for our experimental conditions.²⁷⁻²⁹

Experimental Section

All mass spectra were obtained on a Varian EM-600 mass spectrometer and the GLC analyses were carried out on a Hewlett-Packard 5750 research chromatograph with a 9 m \times 6.25 mm 2,5-hexanedione (20%) on Chromosorb P, 80/100 mesh column operated at 273 K. Gases were handled with standard techniques on a vacuum rack utilizing greaseless stopcocks in all sample preparation areas. Deuterium oxide (Aldrich 100 atom % D), NH₃ (Matheson), and the isomeric butenes (Linde) were degassed and used as supplied. The purity of each isomeric butene was shown to exceed 99.5% by GLC analysis. Phosphorus tribromide (Matheson), cyclohexane (Eastman) and 2-bromobutane (Aldrich) were distilled prior to use.

Deuterium bromide was prepared by the action of D_2O on PBr₃ and purified by trap-to-trap distillation. Infrared analysis showed only trace contamination with HBr. The *erythro-* and *threo-2*-bromo-3-deuteriobutanes were prepared by the radical addition of DBr to *trans-* and *cis-2*butene, respectively, with the reaction temperature maintained at 183 K.²⁰ The labeled bromobutanes were distilled at 10^{-5} mmHg, identified by IR and by solution phase dehydrohalogenation, and showed to be free of butene contamination by GLC. The method for solution-phase dehydrohalogenation of the bromobutanes has been previously described.^{19,26}

Pyrolyses were done in a 332-cm³ quartz vessel contained in an electric furnace maintained at 590 K. The unheated portion of the reactor was 0.9% of the total volume. Measured amounts of reactant and inhibitors were condensed in a side arm attached to the reactor and rapidly vaporized at the beginning of a run. Reaction times varied from 5 to 30 min which correspond to 0.8-9% conversion. Each run was stopped by condensing the products and unchanged starting material at 77 K. The isomeric butenes were separated by GLC until no isomer intercontamination was observed. Percent composition of the olefins was obtained by planimeter measurement of the GLC trace and peak areas were calibrated by using measured amounts of mixtures of known composition. Deuterium content was determined from the M_{56} : M_{57} peak height ratio after the ionization energy had been decreased so that no daugher ions were observed ($\sim 10.5 \text{ eV}$). Correction for the M + 1 contribution was based on the percentage of the M + 1peak (~5%) with undeuterated butenes. No M - 1 ion was observed under these conditions.

Results

For the base-promoted solvolysis, samples of 2-bromobutane, erythro-, and threo-2-bromo-3-deuteriobutane

TABLE II:	Elimination	Percentages	for	Solvolysis ^a
and Pyrolysis	s ^b of Pure er	ythro- and		-
threa.2-Bron	no-3-deuteria	obutane		

material	1-butene	<i>trans-</i> 2-butene	<i>cis</i> - 2-butene	
erythro solvolysis	37.1 ± 1.4	28.6 ± 0.8	34.3 ± 1.0	
threo solvolysis	24.0 ± 1.0	68.6 ± 0.7	7.4 ± 1.0	
undeuterated pyrolysis	38.2 ± 0.3	42.0 ± 0.7	19.7 ± 0.7	
erythro pyrolysis	42.2 ± 2.0	47.5 ± 2.3	10.3 ± 0.7	
threo pyrolysis	49.1 ± 1.9	26.1 ± 1.1	24.8 ± 1.3	

^a These results are for calculations based on the deuterium content (see text). ^b Pyrolysis for 30 min at 590 K corrected for cis-trans isomerization and diasteromeric impurities (see text).

were dehydrobrominated under identical conditions.^{19,26} The measured butene percentage yield and percentage deuteration, Table I, were used to calculate the actual composition of the erythro-rich and threo-rich samples. The procedure^{20,26} involved simultaneous solution of 12 analytical expressions relating the composition of the bromobutane samples and butene percentage yield from *pure* diastereomers to the experimental olefin yields and deuterium content. The erythro-rich sample contained 2.5 mol % threo and 7.6% bromobutane- d_0 . Threo-rich samples contained 5.1% erythro and 5.5% bromobutane- d_0 . These are similar to the impurity levels reported by Bartsch.²⁰ For solvolysis of pure diastereomers the expected butene percentage yields calculated from the above procedure are given in Table II.

For the thermal dehydrobromination in the gas phase, the quartz reactor was seasoned with *cis*-2-butene.²¹ GLC analysis of pure butenes pyrolyzed for 30 min showed that surface reactions were completely retarded. Cyclohexene and ammonia were used to inhibit the HBr (DBr) catalyzed isomerization of the butenes. Ammonia greatly reduced the 1-butene to 2-butene reaction, but had little effect on the *cis*-2-butene to *trans*-2-butene isomerization reaction. The effect of NH₃ on the vessel surface was permanent since isomerization in the absence of inhibitors was decreased after the runs with ammonia.

The amount of cyclohexene required to achieve maximum inhibition and the degree of isomerization occurring under conditions of maximum inhibition were determined by pyrolyzing for 30 min equal molar mixtures of HBr, and either *cis*-2-butene or *trans*-2-butene with varying amounts of cyclohexene. Figure 1 shows that a fivefold excess of cyclohexene reduces the isomerization to 1-butene to less than 0.5%. The 2-butene was replaced by 1-butene and the series of experiments were repeated. The data are not shown but a sixfold excess of cyclohexene relative to 1-butene reduced the isomerization to 2-butenes to less than 0.3%. Apparently, the 1-butene to 2-butene interconversion can be suppressed to a negligible level by small quantities of cyclohexene.

Unfortunately, the *cis-trans* interconversion is not as readily controlled. Figure 1 shows that even for an 80-fold or greater excess of cyclohexene $11.4 \pm 1.6\%$ of the *cis-*

TABLE III: Experimental Percentage Yield and Percentage Deuterium Content of 1-Butene, trans-2-Butene, and and cis-Butene from Uninhibited and Maximally Inhibited Pyrolysis^a of threo- and erythro-2-Bromo-3-deuteriobutane and 2-Bromobutane- d_0

bromobutane isomer	1-butene		trans-2-butene		cis-2-butene		trans 2 hutana
	% yield ^b	% deuteration ^c	% yield ^b	% deuteration ^c	% yield ^b	% deuteration ^c	cis-2-butene
			A. Uninh	ibited Pyrolysis			
undeuterated	34.1 ± 0.3^{d}		39.8 ± 0.6	• •	26.1 ± 0.4		1.52 ± 0.05
threo ^e	47.6 ± 1.9		30.9 ± 1.3		21.5 ± 2.0		1.44 ± 0.06
erythro ^f	41.7 ± 2.0		36.8 ± 1.2		21.5 ± 2.0		1.71 ± 0.09
		B.	Maximally	Inhibited Pyrolys	is		
undeuterated	38.2 ± 0.3		41.0 ± 0.7		20.8 ± 0.7		1.98 ± 0.10
threo ^e	48.1 ± 1.9	95.8 ± 0.8	28.6 ± 1.1	19.1 ± 1.0	23.2 ± 1.3	88.6 ± 0.5	1.23 ± 0.10
erythro ^f	42.1 ± 2.0	95.0 ± 1.1	44.2 ± 2.2	90.2 ± 0.5	13.8 ± 0.7	26.4 ± 1.2	3.20 ± 0.10

^a Pyrolysis for 30 min at 590 K. This mean percentage conversion was $8.3 \pm 1.1\%$. ^b Average of 10 GLC traces. ^c Average of 5-15 MS traces. ^d Standard deviation. ^e Sample rich in *threo*-2-bromo-3-deuteriobutane; see text for actual composition. ^f Sample rich in *erythro*-2-bromo-3-deuteriobutane; see text for actual composition.



Figure 1. Experimental butene percentage yields for the pyrolysis of *cis*-2-butene [1-butene (O) and *trans*-2-butene (\Box)] and for the pyrolysis of *trans*-2-butene [1-butene (\bullet) and *cis*-2-butene (\blacktriangle)] vs. the cyclohexene/hydrogen bromide ratio. The circles are means of multiple analyses and the half-filled circles represent 1-butene percentage yields that were the same for pyrolysis of *cis*-2-butene and *trans*-2-butene. Pyrolysis times were 30 min at 590 K.

2-butene was converted to *trans*-2-butene, and $7.9 \pm 1.2\%$ of the trans isomerized to cis. The results that are presented next indicated that an 80-fold excess of cyclohexene in Figure 1 corresponds to the onset of maximum inhibition.

A series of pyrolyses were performed with *erythro*- or *threo*-2-bromo-3-deuteriobutane and varying amounts of cyclohexene, Figures 2 and 3, respectively. Pyrolyses times of 8–60 min were found to give different degrees of conversion of erythro or threo to the olefins but had little affect on the olefin percentage yield for a constant fraction of cyclohexene.

Since isomerization between 1-butene and the 2-butenes is unimportant, the observed *trans*-2-butene:*cis*-2-butene ratio was a more sensitive measure of isomerization than the percentage of either *trans*-2-butene or *cis*-2-butene alone. Figure 4 shows the pronounced effect of cyclohexene on the *trans*-2-butene:*cis*-2-butene ratios. For cyclohexene:2-bromobutane- d_1 ratios greater than approximately 6:1 the trans:cis ratios were constant, indicating that the point of maximum inhibition had been reached. Pyrolyses for 30 min gave $8.3 \pm 1.1\%$ conversion to the olefins. Therefore, to determine the inhibitor:olefin ratio at the end of a pyrolysis the abscissa in Figures 2-4 must be multiplied by approximately 12. Thus, the onset of maximum inhibition in Figures 2-4 corresponds to cyclohexene:butene $\approx 70:1$. If we assume that maximum



Figure 2. Experimental butene percentage yields [1-butene (O), *trans*-2-butene (\blacktriangle), and cis-2-butene (\square)] vs. the cyclohexene/*er*-*ythro*-2-bromo-3-deuterlobutane ratio.



Figure 3. Experimental butene percentage yields [1-butene (O), *trans*-2-butene (\blacktriangle), and *cis*-2-butene (\square)] vs. the cyclohexene/ *threo*-2-bromo-3-deuteriobutane ratio.

inhibition is achieved with cyclohexane:butene > 70:1 then Figure 1 shows that $11.4 \pm 1.6\%$ cis to trans and $7.9 \pm 1.2\%$ trans to cis isomerization remains in a maximally inhibited system. This observation is important since some deuterium scrambling occurred even for maximum inhibition and the mass spectra data are expected to reflect this scrambling.

Table III gives the experimental butene percentage yields for 30-min pyrolyses of 2-bromobutane- d_0 and threo-rich and erythro-rich samples of 2-bromo-3-deuteriobutane with no added cyclohexene and with a





Figure 4. Experimental [*trans*-2-butene]/[*cis*-2-butene] for 30-min pyrolysis at 590 K of *threo*- (□) and *erythro*-2-bromo-3-deuteriobutane (O).

6-fold or greater excess (maximum inhibition) of cyclohexene. The trans:cis ratio is included and the marked difference for threo and erythro should be noted. The measured percentage deuteration for 1-butene, *cis*-2-butene, and *trans*-2-butene for maximum inhibition are also given in Table III.

Discussion

Product Yields and the Isomerization Mechanism for the Butene Isomers. Three thermal decomposition studies²⁷⁻²⁹ with 2-bromobutane have been reported, although this work is the first with maximum inhibition of the hydrogen halide catalyzed butene isomerization reaction. Maccoll and Stone²⁸ reported percentage yields of the butene isomers using ammonia as an inhibitor. Since an excess of ammonia was found²⁸ to arrest the 1-butene to 2-butene conversion the close agreement between the 1butene percentage given by the ammonia study, 36.2% (615 K), and our 38.2% (590 K) for an excess of cyclohexene is anticipated. Without inhibitor our 1-butene percentage yield was 4% lower. As expected, the 1-butene percentage from three and erythre is higher than from 2-bromobutane- d_0 since replacement of the H by a deuterium at the 3 position lowers the rate of 2-butene formation. Our trans:cis ratio without inhibitor is 1.52 at 590 K for 2-bromobutane- d_0 , which agrees with the average of 1.58 found by Maccoll and Stone²⁸ over the 563-613 K range. These two values are close to the trans:cis equilibrium ratio of Benson and co-workers,³⁰ 1.55 (604.8 K), and Holmes and Ruo,²² 1.58 (600 K), but higher than the 1.32 (602 K) found by Maccoll and Ross²⁵ at equilibrium. If we accept a value of 1.5, it appears that with no inhibitor the 2-butene ratio from 2-bromobutane is near the equilibrium value even through the relative formation rate is 1.98. The 2-butene isomers are not equilibrated for thermolysis of three (1.44) and erythro (1.71); however, the initial trans:cis ratios are further from equilibrium than for the undeuterated parent.

In the absence of inhibitors, hydrogen bromide catalytically interconverts the butene isomers. For maximum inhibition with cyclohexene, we found that positional rearrangement is quenched but some geometric isomerization remains. A molecular and free radical mechanism^{2.25,31-36} have been postulated for the isomerization

catalyzed by hydrogen bromide. Maccoll and Ross²⁵ suggested a bimolecular process forming a six-membered transition-state complex with exchange of a hydrogen between HBr and butene. This accounts for migration of the double bond but not direct cis-trans rearrangement. Based on deuterium-labeling studies Abell³¹ proposed a free radical mechanism initiated by atomic bromine abstracting hydrogen giving cis or trans allyl radicals. At 590 K thermodynamic equilibrium is reached rapidly since the allyl radical cis-trans isomerization activation energy is less than 20 kcal mol^{-1,32} Abstration of hydrogen by the allyl radials can form both 1- and 2-butene. A third mechanism is bromine atom addition to the double bond followed by rotation about the central carbon-carbon bond and finally expulsion of the bromine.³³⁻³⁶ Only the latter process interchanges just the cis-trans isomers and is likely responsible for the residual geometric isomerization.

Stereochemistry of the Dehydrohalogenation Reaction. For maximum inhibition, the observed trans-2-butene: cis-2-butene ratios were 1.23, 3.20, and 1.98, for threo, erythro, and undeuterated 2-bromobutane, respectively. This marked difference provides evidence that dehydrohalogenation is mainly a syn mechanism; however, the deuterium analysis of the butenes provide firmer evidence for a syn-elimination pathway.

The observed deuterium content was high for cis-2butene formed from threo (88.6%) and for trans for erythro (90.2%). These results agree with Barton's¹⁴ demonstration of a preference for a syn-elimination transition state for the gas-phase dehydrohalogenation of haloalkanes and provide an upper estimate for the contribution of an anti process. For the erythro sample the 7.6% 2-bromobutane impurity contributes to the *trans*-2-butene- d_0 yield. Since the rate of formation of trans should be similar for these two 2-bromobutanes the percentage of anti elimination is estimated to be less than 3%. Based on the deuterium content of cis from the threo sample, which contains 5.5% 2-bromobutane, the percentage anti is less than 6%. This provides an upper limit since the analysis ignores the diastereomeric contaminants; thus, the estimated 3% anti for the erythro sample could be accounted for by the 2.5% three impurity and the 6% anti estimated for the three sample could result from the 5.1% erythro impurity. An additional reason for the loss of deuterium specificity in the 2-butene isomers is that cis-trans isomerization remained even for maximum inhibition. To determine if the impurities in the 2-bromobutane samples and the residual cis-trans interconversion would account for the experimental deuterium percentages without inclusion of the anti mechanism, we calculated the expected 2-butene deuterium percentages assuming exclusive syn elimination. The algorithm involved relating the observed butene percentage yields from 2-bromobutane, erythro-, and threo-2-bromo-3-deuteriobutane, and the actual compositions of the erythro-rich and threo-rich samples (vide supra) to give the butene yields expected from stereochemically and isotopically pure three and erythro. The calculated butene yields are shown in Table II. Next, the expected percentage deuteration of the erythro-rich and threo-rich samples were computed by using the actual

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sample compositions and the butene percentage yields from pure bromobutanes. The degree of cis-trans isomerization was also included; 11.4% for cis to trans and 7.9% for the reverse process. The computed (experimental) percentage deuteration for 1-butene, *cis*-2-butene, and trans-2-butene formed from erythro were 93.7 (95.0), 29.2 (26.4), and 90.1 (90.2); and from three were 95.7 (95.8), 85.8 (88.6), and 16.7 (19.1), respectively. The agreements are within experimental error. Since these corrections gave computed deuterium percentages very close to the observed values, contributions from anti-elimination transition-state complexes may be negligibly small.

Most transition-state models developed for rate constant calculations assume a syn-elimination process but the set of rules formulated by Woodward and Hoffman¹⁶ require an anti mechanism for dehydrohalogenations if the C-H, C-C, and C-X bonding molecular orbitals are only considered. Goddard¹⁸ showed the syn process is "allowed" if three pairs of orbitals are involved; the CX bonding pair of the haloalkane shifts to become an X lone pair of HX, the X lone pair shifts to become an HX bonding pair, and the CH bonding pair moves to become a π -bonding pair. Since the halogen is more electronegative than either C or H, development of the new bonds may not be uniform in which case some ionic character is anticipated in the transition-state complex. This view is consistent with the ion-pair model of Benson and co-workers,³⁷⁻³⁹ the decrease in the Arrhenius activation energy upon alkyl substitution at the α - or β -carbons, and the anchimeric assistance found for alkyl chlorides with a double bond in the β -position.⁴⁰ Molecular orbital theory was used by Hiberty⁹ to calculate potential energy surfaces corresponding to syn elimination and planar and nonplanar anti elimination of HCl from ethyl chloride. The syn mechanism having an activation barrier 9.8 kcal/mol lower than the planar anti energy was favored. This prediction is consistent with our findings. The behavior calculated by Hiberty for the chloride p orbitals mimics the motions suggested by Goddard.¹⁸ Hiberty also noted two chlorine orbitals are involved in the reaction; thus, Woodward-Hoffman rules cannot be used to test the forbiddenness of this process. Calculations by Kato and Morokuma¹⁰ and by Wolf and Hase⁴¹ also predict syn elimination.

Kinetic Isotope Effect and Dynamical Models for the Dehydrohalogenation Reaction. The above analysis provided the butene percentage yields for decomposition of pure 2-bromobutane diastereomers. If we assume that the formation rate of 1-butene from bromobutane was not altered by deuterium substitution in the 3 position, the primary and secondary kinetic isotope effects can be calculated.⁴² The $k_{\rm H}/k_{\rm D}$ was computed from the data listed in Table II by multiplying the 2-butene to 1-butene ratio from bromobutane times the inverse ratio from the deuterated bromobutane. For solvolysis the primary and secondary deuterium isotope effects are 3.60 ± 0.5 and 1.07 \pm 0.14 for erythro, respectively, and 3.2 \pm 0.80 and 0.96 \pm 0.12 for three, respectively. Within our experimental error these $k_{\rm H}/k_{\rm D}$ agree with the results of Bartsch.²⁰ For the gas-phase reaction the primary and secondary β -deuterium isotope effects at 590 K are 2.11 ± 0.31 and 0.98 \pm 0.12 for erythro, respectively, and 2.07 \pm 0.24 and 1.02

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 \pm 0.13 for three, respectively. Similar magnitudes for the combined secondary and primary isotope effect have been found for thermal decomposition of CD₃CH₂Cl (1.9),⁴³ CD₃CD₂Cl (2.0),⁴⁴ CHD₂CD₂Cl (2.1),⁴⁵ CHD₂CD₂Br (2.1),⁴⁵ and CDH_2CH_2Cl (1.7 ± 0.6).⁴³ Although only the latter gives just the primary deuterium isotope effect, close agreement is expected since our results and those of others⁴³ show that thermal equilibrium secondary isotope effects are small.

The kinetic isotope effect has aided in selecting transition-state models for RRKM calculation of the dehydrohalogenation rate constant. Models developed by Setser and co-workers^{1,46,47} assume a four-membered ring defined by the halogen, hydrogen, and two carbons with bond orders of 0.1 (C-H), 0.1 (H-X), 0.9 (C-X), and 1.5 (C-C). The remaining motions are designated as out-ofring and, relative to the activated molecule, adjustment of these vibrational frequencies is usually minor. According to Setser¹ and Blades⁴⁵ the large magnitude of the primary deuterium isotope effect⁴²⁻⁴⁷ suggests the hydrogen in the ring is weakly bound to the carbon. Since the observed chlorine-37 isotope effect is small, little carbonhalogen bond extension is expected.⁴⁸ Based on the thermal rate constants for CH₃CH₂Cl and CH₃CD₂Cl, the secondary α -deuterium isotope effect is 1.01.⁴³ Our results show that the secondary β -deuterium effect is also very small, supporting the assumption that the out-of-ring frequencies resemble those of the activated molecule.

Ionic or polar models were postulated by Maccoll and collaborators^{2,49} and later by Benson's group.³⁷⁻³⁹ Α semi-ion pair suggested by Benson has bond orders of 0.5 for C-H, C-X, and H-X and 1.5 for C-C. Benson's approach provided reasonable estimates of the activation energies and Arrhenius A factors but was less successful at matching kinetic data.^{1,47} More recently, Tschuikow-Roux and co-workers^{50,51} modified the semi-ion pair formulation to include a partial formal charge, retained the C-C and H-X bond orders, and made the C-H and C-X bond orders equal but variable. Typically the C-H and C-X bond orders were 0.25, although the range was 0.03 to 0.36. Compared to the procedure of Setser the polar models have nearly complete carbon-halogen fission and a somewhat tighter C-H bond.

The transition-state configurations calculated by Kato and Morokuma¹⁰ and by Hiberty,⁹ respectively, correlate with bond orders of 0.10 and 0.09 for C-X, 0.38 and 0.42 for C-H, 0.26 and 0.27 for H-X, and 1.7 and 1.80 for C-C. These more closely correspond to ionic models and similar prescriptions did not simultaneously reproduce the observed thermal A factors, chemical activation rate constants, and isotope effects.⁴⁷ However, the use of bond orders assigned to the calculated transition-state structures may underestimate the importance of C-H bending motion, which together with tunneling corrections may give

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agreement with kinetic measurements. Both MO calculations were at the SCF level with 4-31G, or similar, basis sets without configuration interaction.⁵² Electron correlation dramatically alters the computed saddle point geometry for repulsive surfaces;53 for example, the F-H distance increased from 1.06 to 1.37 Å for the F + H_{2} reaction. Higher order terms may similarly effect the dehydrohalogenation geometry, especially since the energy disposal pattern suggests a repulsive potential energy surface.^{3,10,54}

Conclusion

We have verified the hydrogen halide elimination stereochemistry is predominantly syn and shown the anti

contribution is small, perhaps zero. The primary deuterium isotope effect of 2.1 found for threo- and erythro-2-bromo-3-deuteriobutane at 590 K agrees with previous work; the β -deuterium effect was 1.0. These $k_{\rm H}/k_{\rm D}$ values concur with the models of Setser and co-workers but are at variance with ionic models and transition state structures calculated with MO theory. As trajectory or ab initio MO computations including configuration interaction become available the discrepancies may be resolved.

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Registry No. threo-2-Bromo-3-deuteriobutane, 49623-58-7; erythro-2-bromo-3-deuteriobutane, 27849-07-6; cis-2-butene, 590-18-1; trans-2-butene, 624-64-6; deuterium, 7782-39-0.

Orientation of Aromatic Compounds Adsorbed on Platinum Electrodes. The Effect of Temperature

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The adsorption of aromatic compounds on smooth polycrystalline platinum electrodes in aqueous solutions has been studied as a function of temperature. Measurements were made by electrochemical methods using thin-layer cells. Eight compounds were studied: hydroquinone (1), 2,5-dimethylhydroquinone (2), 2,2',5,5'tetrahydroxybiphenyl (3), 1,4-naphthohydroquinone (4), anthraquinone-1,5-disulfonic acid (5), 2,5-dihydroxythiophenol (6), 2,3-dihydroxypyridine (7), and 3,6-dihydroxypyridazine (8). The adsorption isotherms of 1-4, which display stepwise transitions to higher packing density with increasing concentration, are influenced by temperature as follows: (i) the transitions are most sharply defined at low temperatures, near 5 °C; (ii) as the temperature is increased, the packing densities at low concentrations increase, while those at high concentrations decrease; (iii) near room temperature (25 < T < 65 °C), an additional plateau appears; and (iv) the transitions are barely noticeable at 65 °C, the highest temperature studied. The packing density of 8 is lower at 65 °C than at ambient temperatures, but those of 5-7 are virtually temperature independent. The results are discussed in terms of librational motion within an oriented monolayer.

Introduction

Packing density measurements based on thin-layer electrochemical methods have recently demonstrated that aromatic compounds chemisorbed from aqueous solutions onto smooth polycrystalline platinum electrodes adopt various nonrandom orientations.¹⁻⁷ Which orientation is adopted in a particular instance has been shown to depend on adsorbate molecular structure,¹ adsorbate concentration,^{3,4,7} the presence of surface-active anions,² and the pH of the solution; 1-3 chirality of inert substituents affects the packing density but not the orientation.⁷ Other factors such as electrode potential and the nature of the solvent and substrate are expected to influence orientation. The adsorbed species are desorbed very slowly or not at all when placed in contact with the pure solvent; ¹⁻⁸ as such,

they may be regarded as surface organometallic compounds. Orientational transitions observed when the adsorbate concentration was increased^{3,4} or surface-active anions were introduced² suggest that alternative modes of binding exist analogously to well-characterized organometallic complexes.⁹⁻¹¹ Molecular orientation has important implications in the chemistry of adsorbed compounds. For instance, the path of electrochemical oxidation of aromatics chemisorbed on Pt electrodes depends on orientation.5-7

The present article describes the influence of temperature on the packing density and orientation of aromatic compounds adsorbed on smooth polycrystalline Pt electrodes. Eight compounds were studied (Table I). It may be mentioned that a few studies have been reported on the effect of temperature on the reversible adsorption of organic compounds at mercury-electrolyte interfaces.¹²⁻¹⁸ At

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