Activation Volume as a Measure of E2–E1cB Character in Elimination Reactions

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Abstract: Selected examples of second-order elimination reactions of neutral substrates and anionic bases, for which the mechanism is not disputed, have activation volumes which are negative for E2 and positive for E1cB. It is suggested that activation volume provides a continuous scale for evaluation of carbanionic character in reactions having intermediate mechanisms. Values of ΔV^* (ml/mol) for various substrate-(base) pairs are: 1-chloro-2-phenylethane (2,6-dibromo-4-methylphenoxide), −12; 2-bromobutane (ethoxide), −10; 2-chloroethyl phenyl sulfone (acetate), −1; *cis*-β-bromostyrene (isopropoxide), −6; *trans*-β-bromostyrene (isopropoxide), −5; *cis*-dibromoethylene (methoxide) +5; 1-methoxyacenaphthene (*tert*-butoxide), +3; 1-methoxyacenaphthene (*tert*-butoxide + crown ether), +15; diacetone alcohol (hydroxide), +6; mandelonitrile (hydroxide), +12.

Introduction

Although we have many kinds of evidence for the possible involvement of intermediate carbanions in base-catalyzed elimination reactions with second-order kinetics (the E1cB mechanism), some key points of interpretation have been challenged, so that it is still not clear whether this process plays a more or less important role than the simultaneous detachment of proton and leaving group (the E2 mechanism). The points of contention between advocates of the stepwise and concerted mechanisms have recently been discussed by Bordwell.[1]

Two general indicators of the extent of proton transfer in transition states, which have been applied to elimination reactions, are the kinetic isotope effect and the Bronsted β parameter. Where the value of k^H/k^D is large (5–7) as in $ArCH_2CH_2Y$ systems,[2] the E2 mechanism seems probable. For similar substrate systems, the Bronsted parameter ranges from 0.39 to 0.72, as would be expected for the E2 mechanism.[3] The kinetic isotope effect by itself cannot be considered conclusive since an argument has been presented to show that an E1cB reaction could also have a large effect.[4]

The observation of β-hydrogen exchange in certain elimination reactions would seem to be fairly clear evidence for the E1cB mechanism, but doubts have been raised here too. One can easily imagine that some carbanion intermediates might eject the leaving group many times more rapidly than they return to starting material and thus fail to show the exchange. On the other hand, it has been argued that when exchange does occur it might be a side reaction to elimination by the E2 mechanism.[5]

In principle it is possible to distinguish the mechanisms by kinetics since in a buffer solution the rate of the E1cB reaction is proportional to the buffer ratio, but the rate of the E2 reaction should increase as the buffer is made more concentrated at constant ratio. The difficulty with an experimental demonstration is that the lyate ion usually dominates other bases in catalytic effectiveness. Several cases in which the kinetic method appears to have succeeded are discussed in a review.[6]

The Hammett equation has been applied to elimination reactions with the intention of evaluating carbanionic character in the transition state, but the results are confusing. The values of ρ are already fairly large (+2.07 to +3.12)[7] in the series $ArCH_2CH_2Y$ which is thought to display the E2 mechanism, and it is not clear how much larger the value should be for the E1cB mechanism. For the reactions of phenyl β-chloroethyl sulfones, which are thought to have considerable carbanion character, the values of ρ are actually lower (1.64 to 1.81).[8]

There is a clear need for some measure which will provide a greater range of variation than those discussed above and a clearer physical relationship to the transition state. It is possible that the activation volume may fill this need. We can foresee a large difference in ΔV^* between the concerted mechanism which should have a value near −10 ml/mol and the two-stage mechanism which should have a value near +10. These values are characteristic of bond-making and bond-breaking processes, respectively. For reactions of simple highly symmetrical molecules without change of electrostriction, the activation volume may be estimated a priori by taking the product of the van der Waals cross-sectional area normal to the breaking or forming bond and the change in length resulting from the interconversion of a bond distance and two van der Waals radii.[9] For the reactions under consideration here, this approach is obviously too crude to be useful, but an extensive compilation of experimental determinations[10] shows that activation volumes in this category seldom fall outside of the range 5–15 ml. The total volume change of reaction, which may be estimated from the molar volumes of reactants and products, is usually not much larger.

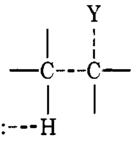
In the present application, it is necessary to make two assumptions which require some justification: (1) there is no significant volume change for the reaction $HA + B^- \rightarrow BH + A^-$; (2) there is no change in the volume of electrostricted solvent. The first is made plausible by considerations of symmetry. The second requires the reaction to conserve ionic charges. For practical purposes, this limits our scope to neutral substrates and anionic bases, but fortunately, this combination is probably the most common. We will need to be mindful of differences in charge delocalization, which in extreme cases can cause electrostrostrictive volume changes almost as great as bond making and bond breaking.

Keeping in mind the known sources of uncertainty such as experimental error, variations in structure, variations in electrostriction, and variations in temperature, it seems reasonable to expect that we can discriminate about five degrees or stages of transition state character with a separation of 5 ml between stages. These might be described as extreme E2, tending to E2, central, tending to E1cB, and extreme E1cB.

Our expectations of the behavior of ΔV^* are strengthened by two previously reported results. For the reaction of 2-bromobutane and ethoxide ion,[11] which is generally considered to be an E2 reaction, the value is −10 ml/mol. For the α-elimination of chloroform with hydroxide ion,[12] which is thought to have the E1cB mechanism, the value is +16 ml/mol. The strongest reason for assigning the E1cB mechanism is that hydrogen exchange is much faster than elimination. The acid–base reaction of chloroform, although studied for many years, is still a subject of interest.[13]

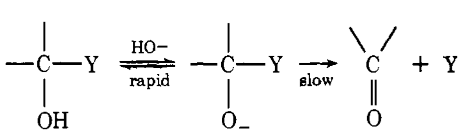
Substantiation of the Method

Since previous work had furnished only one example each of activation volume measurement for the end members of the E2–E1cB spectrum, it seemed necessary to obtain others. The base-promoted elimination of 1-chloro-2-phenylethane seems to be universally accepted as an example of the E2 mechanism.[1] We determined ΔV^* for its reaction with sodium 2,6-dibromo-4-methylphenoxide in Me_2SO. This somewhat unusual base was chosen for reasons of experimental convenience since it has an appropriate base strength and it permits the use of bromine titration for analysis of reaction mixtures. The result, −12 ± 2 ml/mol, is shown in Table I together with the results of measurements on other compounds. The value is appropriate for the E2 mechanism because it reflects a predominant bond making but is not so negative as it would be if there were no bond breaking. In the transition-state structure below, the dotted lines indicate partial bonds.



For second-order reactions of an ion and a neutral molecule in which an intermediate adduct is postulated, and the contribution of bond breaking is presumably slight, e.g., ester and amide hydrolysis and nucleophilic substitution of aryl substrates,[10] the values range from −10 to −20. The blend of bond making and bond breaking in E2 reactions is probably similar to that in SN2 reactions. For several such reactions of 1-bromobutane,[14] the value of ΔV^* ranged from −8 to −12. Although the merged SN2-E2 mechanism[15] has failed some experimental tests,[16] the structural differences between the SN2 and E2 transition states may be slight. For the substitution side reaction of 1-chloro-2-phenylethane we obtained a value of −15 ± 2.

In order to probe the opposite end of the mechanistic spectrum, we selected the elimination of acetone from diacetone alcohol and HCN from mandelonitrile. In these reactions there can be no doubt that removal of the proton is several orders of magnitude faster than ejection of the leaving group.[17] The accepted mechanism is shown below:



$$-\underset{\text{OH}}{\overset{|}{C}}-Y \underset{\text{rapid}}{\overset{\text{HO}^-}{\rightleftharpoons}} -\underset{O^-}{\overset{|}{C}}-Y \xrightarrow[\text{slow}]{} \underset{\text{O}}{\overset{\diagdown\;\diagup}{\underset{\|}{C}}} + Y^-$$

The activation volumes for diacetone alcohol and mandelonitrile are respectively +6 ± 1.5 and +12 ± 2 ml/mol. The values are in harmony with the prediction of +10 ml/mol, which was based on the assumption of no volume change for the preequilibrium and a typical bond-breaking value for the slow step. It is reasonable for mandelonitrile to have a more voluminous (more productlike) transition state than diacetone alcohol because its dissociation constant is smaller, 0.0029 vs 0.039 l./mol.[18] This is in accordance with the Hammond postulate[19] that more endothermic reactions will have more productlike transition states.

It has been reported elsewhere[20] that ΔV^* for diacetone alcohol elimination ranges from −6.6 to +3.8 ml in an interval of 10°C. Such a sensitivity of activation volume to temperature is unmatched by any reaction of any type in le Noble's extensive compilation.[10] We have measured ΔV^* at 15 and 25° and find the same value, +6 ± 1.5 ml.

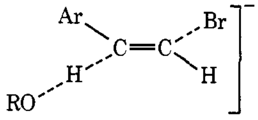
Table I. Activation Volumes (ml/mol) in Order of Expected Increase of E1cB Character

Substrate	Expected mechanistic type	ΔV^*
2-Bromobutane[10]	E2	−10 ± 1
1-Chloro-2-phenylethane	E2	−12 ± 2
cis-β-Bromostyrene	E2	−6 ± 1.5
trans-β-Bromostyrene	Central	−5 ± 1
cis-Dibromoethylene	Central	−5 ± 1
2-Chloroethyl phenyl sulfone	Central	−1 ± 1
1-Methoxyacenaphthene	Central	3 ± 1
1-Methoxyacenaphthene + crown ether	Central	15 ± 3
Diacetone alcohol	E1cB	6 ± 1.5
Mandelonitrile	E1cB	12 ± 2

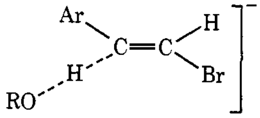
Although it is not usually regarded as an elimination reaction, the decarboxylation of a salt provides a case in which the proton is totally removed in the initial state. Previous determination of ΔV^* for such reactions[21] gave values from +2 to +11 ml/mol. This helps to alleviate concern about the assumption of zero volume change for the proton transfer.

β-Bromostyrene

The mechanism of alkaline dehydrobromination of the isomers of β-bromostyrene and its 4-nitro derivative was first investigated by Cristol,[22] who proposed an E2 transition state for the cis isomer and an E1cB transition state for the trans isomer. His transition state diagrams (I and II) are reproduced below.



I



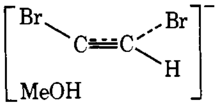
II

Recent work on the *cis*-β-halogenostyrenes[23] has given additional evidence for the E2 mechanism in the form of a significant k^H/k^D ratio (3.2–4.6), absence of hydrogen exchange, and a large leaving group effect. For *cis*-β-bromostyrene with sodium isopropoxide, the activation volume is −6 ± 1.5 ml/mol, which is consistent with structure I, but by comparison with the values of −10 and −11 for the supposedly pure E2 types indicates a leaning toward E1cB. It is not possible to say whether this results from a more complete proton transfer or leaving group detachment or a combination of these effects. At any rate, it is indicated that the transition state is much closer to E2 than E1cB.

For *trans*-β-bromostyrene with sodium isopropoxide, ΔV^* is −5 ± 1 ml/mol, which is inconsistent with an extreme E1cB or even central mechanism. It is thus understandable that hydrogen exchange was not observed. The transition state could be described by structure II with the provision that proton transfer is incomplete and the leaving group has not begun to detach. As in the case of the cis isomer, there is a strong leaning toward E2.

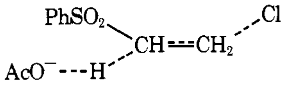
cis-Dibromoethylene

The elimination reaction of *cis*-dibromoethylene with methoxide ion[24] and triethylamine[25] has received a variety of mechanistic tests by Miller and coworkers. The kinetic isotope is very small with both bases, and hydrogen exchange occurs with methoxide at a rate approximately 25 times greater than that of elimination. On these grounds, the E1cB mechanism is proposed. For the reaction with triethylamine, which gives no hydrogen exchange, a slight variant with some ion-pair character $(\mathrm{E1cB})_{\mathrm{ip}}$ is suggested. The latter does not concern us directly because neutral bases are unsuitable for our method of investigation. The activation volume for the reaction with methoxide ion is +5 ml/mol, which is intermediate between the values for the two model E1cB reactions of diacetone alcohol and mandelonitrile. It seems probably that bond breaking has progressed to a considerable degree as depicted below:



2-Chloroethyl Phenyl Sulfone

Several clues to the mechanism of elimination by this substrate have been provided by Yano and Oae.[8] The Hammett ρ value ranges from 1.64 to 1.81, which seems low for a carbanionic transition state, but the authors are not unduly concerned because they say it is a composite of many factors. The $k^{\mathrm{H}}/k^{\mathrm{D}}$ ratio is 2.0 to 2.1, which is intermediate between the values expected for the E2 and E1cB extremes. The leaving group effect is said to be small with Br/Cl 7.0. The Bronsted β parameter is 0.74, which indicates that the proton is extensively transferred. On the basis of this evidence, Yano and Oae assign the mechanism E2cB by which they mean to suggest that proton removal is rate determining rather than ejection of the leaving group. The activation volume for the reaction of 2-chloroethyl phenyl sulfone with acetate ion in alcohol is -1 ± 1 ml/mol. This value is very near the middle of the scale and is consistent with the evidence above. The transition state structure below is intended to suggest that the proton is almost completely removed, and the leaving group is only slightly loosened.



Acetate ion is significantly different from the other bases used in this study inasmuch as the charge is delocalized equally over two atoms, and the electrostriction of solvent is consequently less. Fortunately, the effect is compensated by the presence of an effective electron-withdrawing group in the substrate, so that the somewhat carbanionic transition state will also have subnormal electrostriction. It is difficult to guess how seriously the interpretation of ΔV^* is clouded by these effects, but a purposeful effort by le Noble[26] to demonstrate a delocalization effect showed a variation in ΔV^* of approximately 3 ml/mol.

1-Methoxyacenaphthene

The elimination of methanol from 1-methoxyacenaphthene with catalysis by various *tert*-butoxides in *tert*-butyl alcohol is reported to have the E1cB mechanism.[27] Hydrogen exchange was observed, and the rates were roughly comparable to the rates of elimination. The transition state would therefore appear to be not far beyond the E2 stage. Under certain conditions the elimination was chiefly cis, which was said to be caused by pairing of *tert*-butoxide with its cation. Under these same conditions, the exchange was also primarily cis. Addition of dicyclohexyl-18-crown-6 ether caused the expected shift toward trans exchange and elimination as a consequence of disruption of the ion pairs.

For potassium *tert*-butoxide alone, the activation volume is $+3 \pm 1$ ml/mol, and with addition of dicyclohexyl-18-crown-6 ether, it is $+15 \pm 2$. The latter more nearly conforms to the ideal case of a neutral molecule reacting with an unpaired ion and has the simpler interpretation. The large positive value indicates a high degree of bond breaking, which is perhaps not surprising for such a poor leaving group in the light of the Hammond postulate. The smaller value in the absence of crown ether can be attributed to increased electrostriction caused by charge separation. In the activation process, the transfer of negative charge from oxygen to carbon and away from potassium is probably too rapid for the potassium ion to form a new pair. A decrease of volume accompanying controlled separation of charge in isomeric zwitterions has been demonstrated previously.[28]

Experimental Section

1-Chloro-2-phenylethane. Phenethyl alcohol was refluxed with thionyl chloride for 3 hr and distilled to give a 62% yield of 1-chloro-2-phenylethane, $d^{25}{}_{4}$ 1.069. The reaction mixture was an ethanol solution of 1-chloro-2-phenylethane (0.15 *M*) and sodium 2,6-dibromo-4-methylphenoxide (0.15 *M*). A 10-ml portion was allowed to react at 65.0° for a time estimated to give about 50% reaction (approximately 2 hr), depending on the pressure which ranged from 1 to 1300 bars. The reaction mixture was quenched by adding 10 ml of dilute nitric acid and then extracted with 5 ml of $\mathrm{CCl_4}$. The aqueous layer was titrated with silver nitrate to determine the sum of elimination and substitution products, and the $\mathrm{CCl_4}$ layer was analyzed for styrene by adding an excess of bromine solution and titrating with sodium thiosulfate. A plot of ln k vs. P shows no definite curvature. The mean deviation of points from the best straight line was about 2% for substitution and 6% for elimination.

Diacetone Alcohol. A sample obtained from the Shell Chemical Co. was used to prepare aqueous solutions which were 0.8 *M* in substrate and 0.01 *N* in sodium hydroxide. The dilatometric reaction cell was a 4-ml glass bulb with a neck of capillary tubing having an inner diameter of 1 mm and a length of 70 mm. A quantity of mercury, sufficient to fill the neck almost completely, was placed in the bulb in an upright position, and the cell was then completely filled with reaction mixture. The cell was inverted, and the mercury was shaken into the capillary. The inverted cell was then placed in a test tube with a small pool of mercury in the bottom. The mercury served to transmit the pressure to the reaction mixture and also to determine the volume by measurement of the height of the interface in the capillary. After 10 half-lives, the interface dropped 3.66 ± 0.03 cm. At ordinary pressure and a temperature of 25° we obtained a pseudo-first-order rate constant of 0.283 hr^{-1}, and the best recorded value[18] is 0.280.

Mandelonitrile. The nitrile was prepared by the procedure of Corson.[29] Reaction mixtures were prepared by dissolving 33 mg of nitrile in 1 ml of ethanol and adding 25 ml of an aqueous buffer solution containing acetic acid (0.1 *N*) and sodium acetate (0.1 *N*). Analysis was performed by titration with 0.025 *N* silver nitrate solution. The end point was indicated by the potential of a silver electrode. The effect of pressure on the equilibrium constant was determined by reacting duplicate samples at 36.5° for 1 day at pressures of 30, 680, and 1260 bars. The values at these pressures were, respectively, 0.00299, 0.00231, and 0.00159 *M*. A linear graph of ln K vs. P was used to obtain values at other pressures. The slope gave a value of +14 ml/mol for the volume change of the reaction. The rate constant for elimination was obtained from the equation

$$kt = \frac{K}{R} \ln \frac{K + R + c(K - R)/c_0}{K - R + c(K + R)/c_0} \qquad (1)$$

in which c_0 is the initial concentration of mandelonitrile, c is the concentration at time t, K is the equilibrium constant, and R is the quantity $(4c_0K + K^2)^{1/2}$. At low pressure the concentration of $\mathrm{HO^-}$ is 4.46×10^{-10} *M*, and the rate constant is $9.2 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$. Pressure retards the rate slightly corresponding to an apparent ΔV^* of +2 ml/mol, but it also reduces the pOH because the ionization volumes of water and acetic acid are substantially different. A study of pressure on buffer solutions[30] gives 10 ml for this difference; thus the corrected activation volume is +12 ml. The following fuller explanation is offered. The concentration of $\mathrm{HO^-}$ is governed by the expression:

$$K = (\mathrm{HO^-})(\mathrm{HAc})/(\mathrm{Ac^-}) \qquad (2)$$

The acetic acid and acetate ion are major species, and the ratio $(\mathrm{HAc})/(\mathrm{Ac^-})$ is not significantly affected by pressure; therefore, $\mathrm{d}\ \ln K/\mathrm{d}P = \mathrm{d}\ \ln (\mathrm{HO^-})/\mathrm{d}P = \Delta V/RT = -10\ \mathrm{ml}/RT$. Further-

Table II. Variation of Rate Constant with Pressure

1-Chloro-2-phenylethane (0.15 *M*) and sodium 2,6-dibromo-4-methylphenoxide in ethanol, 65.0°						
Elimination Reaction						
P (bars)		68	544	680	1020	1360
$k \times 10^3$ (M^{-1} sec^{-1})		6.80	7.29	7.65	9.89	12.55
Substitution Reaction						
P (bars)		68	544	680	1020	1360
$k \times 10^2$ (M^{-1} sec^{-1})		2.96	3.92	4.20	4.84	6.06
cis-β-Bromostyrene (0.0143 *M*) and sodium isopropoxide (0.182 *M*) in isopropyl alcohol, 26.0°						
P (bars)	1	218	774	1060	1225	1360
$k \times 10^4$ (M^{-1} sec^{-1})	5.29	5.58	6.00	6.24	6.57	6.85
trans-β-Bromostyrene (0.0158 *M*) and sodium isopropoxide (0.147 *M*) in isopropyl alcohol, 118.0°						
P (bars)	1	208	445	816	1090	1360
$k \times 10^4$ (M^{-1} sec^{-1})	2.19	2.24	2.47	2.53	2.63	2.73
cis-Dibromoethylene (0.018 *M*) and sodium methoxide (0.1055 *M*) in methanol, 37.0°						
P (bars)	1	544	774	92.4	1140	
$k \times 10^4$ (M^{-1} sec^{-1})	8.78	8.00	7.73	7.00	6.80	
2-Chloroethyl phenyl sulfone (0.050 *M*) and sodium acetate (0.050 *M*) in ethanol 50.0°						
P (bars)	1	816	1122	1360		
$k \times 10^3$ (M^{-1} sec^{-1})	1.82	1.89	1.95	1.95		
1-Methoxyacenaphthene (0.064 *M*), and potassium *tert*-butoxide (0.314 *M*) in *tert*-butyl alcohol, 82.0°						
P (bars)	34	707	816	1360		
$k \times 10^5$ (M^{-1} sec^{-1})	6.03	5.45	5.36	5.27		
1-Methoxyacenaphthene (0.064 *M*), dicyclohexyl-18-crown-6 (0.405 *M*), and potassium *tert*-butoxide (0.405 *M*) in *tert*-butyl alcohol, 57.0°						
P (bars)		1		1360		
$k \times 10^4$ (M^{-1} sec^{-1})		2.53 ± 0.25		1.23 ± 0.13		
Diacetone alcohol (0.080 *M*) in aqueous sodium hydroxide (0.0100 *M*), 25.0°						
P (bars)	1	340	680	1360		
k (hr^{-1})	0.285	0.271	0.245	0.204		
Diacetone alcohol (0.080 *M*) in aqueous sodium hydroxide (0.0100 *M*), 15.0°						
P (bars)	1		680		1360	
k (hr^{-1})	0.097		0.088		0.071	
Mandelonitrile (0.0095 *M*), sodium acetate (0.100 *M*), and acetic acid (0.100 *M*) in water, 36.5°						
P (bars)	27	694	714	1090	1260	
K (*M*)	0.002999	0.00231			0.00159	
k (hr^{-1})	0.148	0.136	0.136	0.132	0.127	

more, $\Delta \ln k(\mathrm{HO}^-) = \Delta \ln k + \Delta \ln (\mathrm{HO}^-) = \Delta P(\Delta V^*_{\mathrm{appt}})/RT = P(\Delta V^* - 10\ \mathrm{ml/mol})/RT$.

***cis*-β-Bromostyrene.** The starting material was obtained by decarboxylative elimination of *trans*-cinnamic acid dibromide in total darkness by the method of Cristol and Norris.[22] A 2-propanol solution of the bromide (0.0143 *M*) and sodium isopropoxide (0.182 *M*) was allowed to react at 26.0° and various pressures up to 1300 bars for times near 2 hr. The reaction mixture was analyzed by acidification and titration with silver nitrate solution.

***trans*-β-Bromostyrene.** A commercial sample containing mostly the trans isomer was purified by partial freezing, and a portion melting at 7° was collected. The reaction mixture was similar to that used for the cis isomer, but the temperature was 118.0°.

***cis*-Dibromoethylene.** Debromination of 1,1,2,2-tetrabromoethane by zinc gave a mixture of geometric isomers containing 60% *cis*-dibromoethylene.[31] The isomers were not separated, but the very large difference in rates of elimination made it justifiable to regard the trans isomer as an inert impurity.[31] A methanol solution of dibromide (0.018 *M*) and sodium methoxide (0.106 *M*) was allowed to react at 37.0° for times near 3 hr and at various pressures up to 1140 bars. Analysis was by titration with silver nitrate solution.

2-Chloroethyl Phenyl Sulfone. The sulfone was prepared by the method of Ford-Moore, Peters, and Wakelin.[32] Reaction mixtures were prepared by combining 5 ml of 0.1 *M* sodium acetate in ethanol with 5 ml of 0.1 *M* 2-chloroethyl phenyl sulfone in ethanol. The samples were heated for 2 hr at 50° and analyzed for chloride ion by titration with silver nitrate solution. A 100-ml solution reacted for 10 half-lives under these conditions gave 86% of the theoretical quantity of phenyl vinyl sulfone by gravimetry.

1-Methoxyacenaphthene. The product we obtained from 1-bromoacenaphthene by the method of Hunter[27] contained much acenaphthylene, so we elected to methylate 1-acenaphthenol. A solution of 10.1 g of 1-acenaphthenol[33] in 30 ml of 1,2-dimethoxyethane was treated first with 2.85 g of NaH suspension (57%) until the evolution of hydrogen ceased and then with 4.7 ml of iodomethane. After 1 day at room temperature, the solvent was evaporated, and the residue was taken up in ether, dried, and distilled. We obtained 9.56 g (85%) of the ether, bp$_2$ 135-145°. Reaction mixtures were prepared by transferring about 30 mg of 1-methoxyacenaphthene to the sample cell, weighing by difference, and adding a 2-ml portion of potassium *tert*-butoxide (0.314 *M*) in *tert*-butyl alcohol. The samples were allowed to react for several hours at 82.0° and analyzed by measurement of the absorbance at 331 nm after dilution to 250 ml with ethanol. The molar extinction coefficients for acenaphthylene and 1-methoxyacenaphthene are, respectively, 3800 and 94.

Solutions containing 1-methoxyacenaphthene and equal concentrations of dicyclohexyl-18-crown-6 and potassium *tert*-butoxide (0.405 *M*) in *tert*-butyl alcohol were prepared and analyzed as above after reaction at 57.0°.

High-Pressure Apparatus. An Aminco Micro Series reactor and hand-operated hydraulic pump were used. The temperature was stabilized by a 200-lb ingot of aluminum which had been bored to fit the reactor snugly. An oil film provided good thermal contact. The temperature was controlled within 0.05°. Reaction mixtures were contained in a glass bell which was inverted after filling with mercury. A pool of mercury outside the bell provided a seal and transmitted pressure from the hydraulic fluid.

Calculation of Activation Volumes. The logarithm of the ratio of the rate constant at high pressure to the rate constant at atmospheric pressure was plotted against pressure, and the best straight line was drawn through the origin and other points. The slope was used to calculate the activation volume according to the equation

$$-RT(\partial \ln k/\partial P)_T = \Delta V^*$$

Acknowledgment. The authors are indebted to the National Science Foundation for support of this work.

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