

of Klages.⁶⁵ To calculate the enthalpy of formation of isopropyl fluoride, the enthalpy of hydrogenation of isopropyl fluoride to propane and hydrogen fluoride at 248°⁶⁶ was used. The heat capacities of hydrogen,⁶⁰ hydrogen fluoride,⁶⁰ propane,²⁸ and isopropyl fluoride⁶⁷ at 25° were used to calculate the enthalpy of hydrogenation at 25°.⁶⁸ This value (−20.69 kcal./mole) led to the value −68.33 kcal./mole for the heat of formation of isopropyl fluoride. Entropies of diethyl ether, diisopropyl ether, and methyl ethyl ketone were calculated from the Benson and Buss rule of additivity of group properties and those of anisole,⁶⁹ *t*-butyl hydroperoxide, di-*t*-butyl peroxide, thiophenol,⁶⁹ thioanisole,⁶⁹ isobutyronitrile,⁷⁰ and isopropyl fluoride from their rule of additivity of bond contributions.⁶³ The entropy values listed by Benson and Buss were used for hydrogen peroxide, methyl mercaptan, and dimethyl sulfide.⁶³

Reported values for the solubility of diethyl ether,⁷¹ diisopropyl ether,⁷² anisole,⁷³ hydrogen sulfide,⁷⁴ hy-

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(67) The value 19.48 cal. deg.⁻¹ mole was calculated by the method of adding bond contributions.⁶³

(68) The use of constant heat capacities over the temperature range 25–248° is based on the approximation that the heat capacities of propane and isopropyl fluoride will increase by the same amount over this range. Changes in the relative heat capacities of hydrogen and hydrogen fluoride will be negligible.

(69) Since the Ph-H and Ph-C bond contributions are 1.2 and 1.0 e.u. lower than the C-H and C-C bond contributions, it was assumed that the Ph-O and Ph-S bond contributions are 1.1 e.u. lower than the C-O and C-S contributions, respectively. With the Ph-O contribution thus obtained the entropy of phenol may be calculated with an error of only 0.56 e.u.

(70) This value (74.8 e.u.) was calculated by adding to the entropy of acetonitrile⁶⁰ the contributions for two more C-C bonds and four more C-H bonds and making the symmetry number correction.

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drogen,⁷⁵ and methane⁷⁶ in water at 25°, and for the vapor pressures of pure water, diethyl ether,⁷¹ diisopropyl ether,⁷⁷ and dimethyl sulfide⁷⁸ at 25° were used. The vapor pressure of thiophenol was calculated from an equation derived from data at higher temperatures,⁷⁹ and that of thioanisole from its boiling point⁸⁰ and Dreisbach's Cox chart No. 10.⁸¹ For methanol and ethanol, solutions of the concentrations shown are reported to have the partial pressures of alcohol shown in Table III.⁷¹ It was assumed that the partial pressure of hydrogen cyanide over a 1.83 *M* solution at 18°⁷¹ increases by the same factor that the vapor pressure of pure hydrogen cyanide does⁷¹ when the temperature is increased to 25°. The partial pressure of acetonitrile was calculated by interpolation and extrapolation from data on solutions of similar concentration at 20 and 30°.⁷¹ Data on the partial pressures of isopropyl alcohol,⁸² phenol,⁷¹ acetone,⁷¹ and methyl ethyl ketone⁷¹ at concentrations near those shown in Table III and temperatures in the area 35–90° were adjusted to a common concentration and a plot of $\log p$ vs. $1/T$ was prepared. From the resultant slightly curved lines the partial pressure at 25° was estimated by extrapolation.

Acknowledgment. We wish to acknowledge our indebtedness to the National Science Foundation and the Charles F. Kettering Foundation for grants that made possible the purchase of the ultraviolet-visible spectrophotometer used in this investigation.

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The Volume of Activation in Elimination Reactions

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Volumes of activation have been measured for E1 and E2 reactions of neutral and ionic substrates. The transition states for elimination and substitution are almost equal in volume for every combination of charge-type and mechanism. The transition states for the formation of Hofmann and Saytzeff products from a common starting material are also equal within experimental error. The results permit inferences concerning the nature of the bonding in the transition states.

Introduction

In recent years there has been great interest in the detection of the structural details of transition states

in olefin-forming elimination reactions. Two relatively new and promising methods of investigation are the solvent isotope effect¹ and heavy element isotope effects.² Still another research tool as yet not applied to elimination reactions is the determination of volumes of activation by measurement of the effect of hydrostatic pressure on reaction rates. The application of this technique to the study of organic reaction mechanisms has been recently reviewed.³

The work reported here was directed to three prin-

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cipal objectives. The first was to determine whether the volumes of activation are consistent with expectations based on the currently accepted mechanisms, and then to define roughly the position of the transition states on their reaction coordinates by the method of solvent variation.⁴ The second was to seek evidence on the question whether concurrent E1 and S_N1 reactions pass through the same transition state. If pressure influences the ratio of rates, then the transition states must be different. The third aim was to determine whether the proportion of Hofmann to Saytzeff product in E2 reactions is sensitive to pressure, as one might expect if relief of steric strain is important to the former.

Results and Discussion

Unimolecular Elimination by a Neutral Substrate. The reaction chosen to exemplify this type was the solvolysis of *t*-amyl chloride in 80% aqueous ethanol and 80% aqueous methanol. The procedures were similar to those of Ingold, *et al.*,⁵ except that gas chromatography was used to find the proportions of 2-methyl-1-butene and 2-methyl-2-butene.

The volume of activation based on the rate of appearance of hydrochloric acid is -18 ml./mole as shown in Table I. This determination agrees well with the value of -16 ml./mole calculated from the data of David and Hamann⁶ for the solvolysis of *t*-butyl chloride in 80% aqueous ethanol. A number of other first-order solvolyses of alkyl halides also have large negative volumes of activation.⁷ It is widely believed that the constriction is due to the attraction of solvent by the largely ionic transition state. The ionization of amines in water, for example, leads to a contraction of 21-27 ml./mole.⁸

Table I

Reaction	Solvent	Temp., °C.	ΔV^* , ml.
<i>t</i> -Amyl chloride solvolysis	Ethanol (80%)	34.2°	-18
	Methanol (80%)	29.8°	-16
<i>t</i> -Amyldimethylsulfonium iodide solvolysis	Ethanol (80%)	53.8°	+14
2-Bromobutane and NaOEt	Ethanol	47.8°	-10
<i>t</i> -Amyltrimethylammonium iodide and KOH	Ethanol	84.8°	+15
Triethylsulfonium bromide and NaOH	Water	109.0°	+11 ^a +8 ^b
Triethylsulfonium bromide and NaOCH ₃	Methanol	50.9°	+15 ^a
Tetraethylammonium bromide and NaOCH ₃	Methanol	104.8°	+20

^a Elimination. ^b Substitution.

In order to find the place of the transition state on the reaction coordinate, one may compare the volume of activation with the change of volume associated with the formation of the intermediate carbonium ion.

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Although direct measurement of the latter is impossible, it may be estimated roughly by summing the volume associated with bond rupture and the volume of solvent constricted by a pair of ions. For several unimolecular decompositions in which no new ions are produced, the volume of activation ranges from 9 to 16 ml./mole.^{4,9} If these values are combined with the volumes of ionization of amines mentioned above, the extreme limits are -5 to -16 ml./mole. The value of -18 ml./mole for the volume of activation thus indicates that the transition state is almost completely ionized. It must be admitted that the solvent is only 44 mole % water rather than pure water, although 60 mole % water behaves like pure water with respect to electrostriction by ions.⁴

There is a growing body of evidence that the nature of the starting materials has an important bearing on the distribution of products in reactions which are believed to involve carbonium ion intermediates.¹⁰ The transition states are thereby shown to be non-identical. In an effort to learn whether the transition states for the conversion of *t*-amyl chloride to olefin and substitution product have different molar volumes, we determined the proportions of products at ordinary pressure and 1360 atm. In 80% aqueous methanol the combined olefins accounted for 27 and 24% of the products at low and high pressure, respectively. This difference is about twice the anticipated experimental error, and is probably not significant. When the experiment was repeated using 80% aqueous ethanol, the product was 48% olefin at both pressures. Furthermore, the proportions of the two olefins remained nearly unchanged at 20-22% 2-methyl-1-butene and 78-80% 2-methyl-2-butene. We have therefore not found any evidence of nonidentity of the transition states so far as their volumes are concerned.

Unimolecular Elimination by an Ionic Substrate. The substance selected for testing was *t*-amyldimethylsulfonium iodide, for which a considerable body of kinetic data is available in the literature. The ratio of olefin to dimethyl sulfide is insensitive to pressure within experimental error, and the fraction of 2-methyl-1-butene in the olefins was 23% at 1360 atm. and 21% at 1 atm. The average of these two figures, 22%, is nearly identical with the average of 21% obtained for the solvolysis of *t*-amyl chloride in the same solvent, 80% aqueous methanol. Ingold and co-workers⁵ report 18% terminal olefin for slightly different reaction conditions.

The volume of activation for all reaction pathways is +14 ml./mole, which is surprisingly larger than the value of +10 ml./mole reported for the decomposition of *t*-butyldimethylsulfonium iodide in alcohol.⁴ It must indeed be the second largest positive volume of activation ever reported for a unimolecular process.^{9b} In the case of *t*-butyldimethylsulfonium iodide it was shown that desolvation by dispersal of charge in the transition state is not an important factor, and the positive volume reflects the expansion of the ion along the axis of the breaking C-S bond. If the increase of volume were ascribed to the creation of a cubical void

(9) (a) K. R. Brower, *ibid.*, **82**, 4535 (1960); (b) W. J. le Noble and M. Duffy, *ibid.*, **86**, 4512 (1964).

(10) D. J. Cram and R. V. Sahyun, *ibid.*, **85**, 1257 (1963).

between the *t*-amyl cation and the leaving group, its linear dimension would be 2.8 Å. The energy of a covalent bond enlarged to such a degree would certainly be very small.

Another approach to the estimation of the degree of bond breakage is to compare the volume of activation with the change of volume accompanying a model reaction of the type $A \rightleftharpoons B + C$. We have not been able to devise a practical system in which a univalent ion appears on both sides, but there are many suitable combinations of neutral substances. Three random examples are the dehydration of 2-pentanol (+17 ml.), the elimination of methanol from methyl *n*-amyl ether (+15 ml.), and the dissociation of acetone cyanohydrin (+21 ml.). In this light also, the 14-ml. volume of activation indicates a nearly complete bond rupture.

Bimolecular Elimination by a Neutral Substrate. The reaction of 2-bromobutane with sodium ethoxide in ethanol was selected for study because it is structurally simple and yet it provides an opportunity to observe an effect of pressure on the distribution of isomeric products. Furthermore, the E1 reaction can be easily suppressed. There is competition from the SN2 process; but fortunately, pressures up to 1360 atm. had no measurable effect on the fraction of elimination which remained constant at 65–67%. It was also found that the composition of olefinic product remained invariant at 18–20% 1-butene, 63–64% *trans*-2-butene, and 16–18% *cis*-2-butene. All transition states derived from this reactant combination therefore have the same volume within experimental error.

The volume of activation in 1 *M* sodium ethoxide was –10 ml./mole. Volumes in this range seem to be typical of a variety of bimolecular reactions in which no ions are produced or destroyed and in which the electrostriction of solvent may therefore be presumed not to vary with position on the reaction coordinate. A tabulation of 17 such reactions¹¹ shows a range of –5 to –13 ml. and a mean of –8.3 ml. The closely analogous reactions of *n*-butyl bromide with sodium phenoxide and potassium 2-pyridoxide shows a range from –8 to –12 ml. and a small variation with solvent polarity.⁴ The conclusion to be drawn is that the activation process for all of these reactions is dominated by bond making rather than bond breaking. It is interesting to note that opposite and nearly equal volumes of activation are found for processes dominated by bond breaking, namely, the unimolecular decomposition of diazonium ions^{9a} and sulfonium ions.

In order to infer the structure of the transition state for the E2 reaction of 2-bromobutane, it is useful to consider two extreme cases. If the transition state resembles the products, then the volume of activation would range up to +10 ml./mole, which is the calculated volume change for the reaction below using the



recorded values for the molar volumes of 2-bromobutane and 2-butene, and the partial molar volumes of sodium bromide¹² and sodium methoxide¹³ in meth-

anol, and neglecting the volumes of mixing of the nonionic components. On the other hand, if bond making is nearly complete and bond breaking scarcely begun, the volume change would be roughly –15 to –20 ml./mole on the basis of the models outlined in the preceding section. Since the experimental volume of activation is –10 ml./mole, it is apparent that the transition state resembles an adduct of the starting materials, and that bond rupture cannot have progressed very far.

Bimolecular Elimination by Ionic Substrates. The substances studied were *t*-amyltrimethylammonium iodide in 4 *M* alcoholic potassium hydroxide, tetraethylammonium bromide and sodium methoxide in methanol, and triethylsulfonium bromide with sodium methoxide in methanol. An attempt to work with *t*-amyltrimethylsulfonium iodide was abandoned because of difficulty in suppressing the unimolecular decomposition. In aqueous alkali the triethylsulfonium ion consumed base a little more than two times faster than it produced ethylene, and it was presumed that the SN2 reaction competes. Separate rate constants were found for the two reactions, and the volumes of activation were +8 ml./mole for substitution and +11 ml./mole for elimination. The former is close to the value of +7 ml. found for both trimethylphenylammonium ion and trimethylsulfonium ion with phenoxide ion in water.⁴ The triethylsulfonium ion with methanolic sodium methoxide gave 30% substitution product, and the percentage was the same at high and low pressure. This result is difficult to reconcile with the report that in 60% aqueous ethanol triethylsulfonium hydroxide gives ethylene quantitatively,²¹ but we have confidence in our analytical methods as a result of finding 100% yield of ethylene from tetraethylammonium ion (see below). The volume of activation for elimination is +15 ml./mole, and for substitution it is the same with more than twice as much uncertainty. Tetraethylammonium ion consumed base and produced ethylene at the same rate. Its volume of activation was +20 ml./mole and that of *t*-amyltrimethylammonium ion was +15 ml./mole.

The proportion of Hofmann to Saytzeff product from *t*-amyltrimethylammonium ion remained invariant with pressure at 90% 2-methyl-1-butene and 10% 2-methyl-2-butene. The transition states for their formation therefore have the same volume within 1 ml./mole. Although it is very difficult to estimate *a priori* the difference of volume caused by the different steric compressions of the two transition states, the magnitude might be comparable to the difference in molar volume of the products. According to published densities 2-methyl-1-butene is larger than 2-methyl-2-butene by 2.0 ml./mole, and 1-pentene is larger than 2-pentene by 2.4 ml./mole. The failure to find a difference in volume of activation either for the *t*-amyl or the *sec*-amyl substrate therefore favors the theory of Ingold¹⁴ over that of Schramm¹⁵ for the explanation of the Hofmann rule.

Two quite different pictures of the transition state are consistent with the observed volumes of activation. The simpler and more appealing of these is based upon

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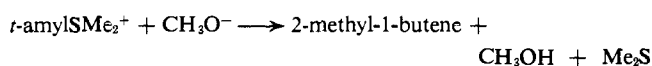
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the close parallel between the volumes of activation for elimination and substitution. For example, the substitution reaction of trimethylsulfonium phenoxide has molar activation volumes of +12 ml. in ethanol and +7 ml. in water,⁴ which agree reasonably with +15 ml. in methanol and +11 ml. in water for elimination by triethylsulfonium ion. Similarly, for substitution on trimethylphenylammonium ion by phenoxide ion the activation volume is +18 ml./mole in ethanol, whereas for elimination by *t*-amyltrimethylammonium ion in ethanol and tetraethylammonium ion in methanol the values are +16 and +20, respectively. It is therefore tenable that the transition states for elimination and substitution are alike in two major respects: (1) the space between nucleophile and substrate has been squeezed out so that the system contracts 10 ml./mole and (2) the ionic charges are almost neutralized, with release of solvent amounting in the extreme case to 25 ml. of water or 40 ml. of ethanol or methanol. The net change is 15–30 ml., which agrees tolerably with the observed volumes of activation. If the leaving group and conjugate acid of the base were physically separated from the olefin in addition to being electrically neutralized, the change of volume would be considerably greater. For methanol one might estimate that 40 ml. of solvent would be released and 20 ml. of intermolecular space would be created, so that the volume change of reaction would be +60 ml./mole. For the following reaction, a change of 74 ml. has been calculated from the densities of solutions containing starting materials and products in methanol at concentrations of 0.50 *M*.



In the alternative picture of the transition state, the base has captured a proton from the substrate and rebounded to normal intermolecular distance. Bond breaking has not commenced in the now zwitterionic substrate. The volume of activation in this case would be entirely due to solvent release. The change of volume could be estimated from a knowledge of the electrostriction produced by stable zwitterions, which in turn can be obtained from the difference of the partial molar volumes of some amino acids and their neutral structural isomers.¹⁶ The required datum is 13–15 ml. of water, which indicates that 10–12 ml. would be released by converting two separate ions into a zwitterion and a neutral molecule. The quantity is commensurate with the volumes of activation.

From the standpoint of designing a critical experiment it is unfortunate that both pictures presented here are consistent with the recent report that kinetic isotope effects indicate a nearly complete proton transfer for elimination reactions of “onium ions”.¹ Both are also consistent with ρ -values for β -phenethyl compounds¹⁷ since a double bond mimics the effects of anionic carbon.

Experimental

Apparatus. The high-pressure equipment, sampling technique, and general approach to measurement of rate constants have been described before.^{4,18}

(16) F. T. Gucker, Jr., I. M. Klotz, and T. W. Allen, *Chem. Rev.*, **30**, 181 (1942).

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Errors. The mean deviation of duplicate rate measurements is usually about 3%. The error in the volume of activation is 1 ml./mole, and it arises almost entirely from the 6% uncertainty in $\ln(k_p/k_0)$. Temperatures were controlled within 0.05° and pressures within 7 atm. All proportional errors in the rate constants, such as those introduced by inert impurities in the starting materials (inaccurate standardizations, calibrations, etc.), are canceled when the volume of activation is calculated.

Solvents. The ethanol was anhydrous, U.S.P. reagent quality and the methanol was Van Waters and Rogers 99.8% grade. The term, 80% ethanol, refers to a mixture of 4 volumes of ethanol with 1 volume of water.

Halides. *t*-Amyl chloride and 2-bromobutane were obtained from Distillation Products Industries and used without purification.

Sulfonium Salts. *t*-Amyldimethylsulfonium iodide was prepared by the reaction of dimethyl sulfide with *t*-amyl iodide,¹⁹ and triethylsulfonium bromide was obtained from diethyl sulfide and ethyl bromide by a modification of a procedure using ethyl iodide.²⁰ The yield of triethylsulfonium bromide after 2 weeks at room temperature was 56%, m.p. 195–197° dec.

Ammonium Salts. *t*-Amyltrimethylammonium iodide, m.p. 225° dec., was prepared by the method of Grovensten, *et al.*,²¹ from *t*-amyltrimethylamine. *t*-Amylamine²² was converted to *t*-amyltrimethylamine by the method of Meiners, *et al.*²³ Tetraethylammonium bromide, m.p. 305° dec., was prepared in 80% yield by treating 22 g. of ethyl bromide with 20 g. of triethylamine in 40 ml. of methanol for 1 week at room temperature.

Gas Chromatographic Analyses. The composition of the olefinic products derived from 2-bromobutane, *t*-amyl chloride, *t*-amyltrimethylsulfonium iodide, and *t*-amyltrimethylammonium iodide was determined by measurement of the areas under the recorder trace. Accurate calibrations were not prepared since the datum required was the precise (not necessarily accurate) ratio of Hofmann to Saytzeff product obtained from the peak areas of the same gas chromatogram. We sought only the effect of pressure on this ratio. The compositions reported here are based on the assumption that structural isomers have the same calibration factor.

The analysis for amylenes began with an extraction of the reaction mixture with carbon tetrachloride (see below). A small portion of the extract was injected into a Beckman GC-2 fitted with a silicone grease column, No. 70158, at 40° with 30 p.s.i. of helium carrier gas. The Hofmann and Saytzeff products were well separated and identified by comparison of the retention times with authentic samples.

The butylene gases were displaced from the reaction mixture by injection of water from a hypodermic syringe

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(23) A. F. Meiners, C. Bolze, A. L. Scherer, and F. V. Morriss, *J. Org. Chem.*, **23**, 1122 (1958).

through a rubber plug in the top of the reaction cell. Samples of the gas were then withdrawn for gas chromatographic analysis with a 10-ft. hexadecane column at ambient temperature. 1-Butene was separated from the 2-butenes, and the *cis* and *trans* isomers were partially resolved. The peak for *cis*-2-butene was identified by comparison with an authentic sample obtained from the Phillips Petroleum Co., and a similar comparison was drawn for 1-butene of which a small sample was obtained by injecting 0.5 ml. of 1-bromobutane into a suspension of 1.0 g. of sodium methoxide in 3 ml. of dimethyl sulfoxide in the reaction cell described above. The major peak was identified as *trans*-2-butene by the characteristic infrared band at 10.4μ .²⁴

Determination of Total Amylenes and Butylenes. The classical method of titration with bromine was adapted to a small scale. A 2-ml. hypodermic syringe was used to pipet a 1-ml. sample of reaction mixture into a 5-ml. glass syringe together with 2 ml. of water and 1 ml. of carbon tetrachloride. The mixture was shaken and the layers were separated. The carbon tetrachloride layer was expressed into a small separatory funnel and treated with 2 ml. of 0.8 *M* Br₂ in CCl₄. After 1 min. the mixture was shaken with 2 ml. of 1 *M* NaI and titrated with standard sodium thiosulfate solution. At each determination a blank was also run. A second extraction of reaction mixture gave a negligible titer.

Determination of Ethylene. Since the reaction mixtures will not dissolve much ethylene at ordinary pressure, a volumetric method was developed. The reactions were carried out in an inverted glass bell which was calibrated as a gas buret. After being withdrawn from the high-pressure reactor, the sample was shaken to prevent supersaturation, and the volume of ethylene (typically 8 ml.) was measured at 22°. The amount of dissolved ethylene was determined by finding the time at which the first small bubble appeared. Since the approximate rate constant was known from more extensively reacted samples, the amount of ethylene needed to produce the first bubble could be calculated. The methanol solutions dissolved 2.5 volumes of ethylene at 22° (650 mm.), and the aqueous media dissolved 1.0 volume. A correction for the vapor pressure of the solvent was also applied. In the case of aqueous triethylsulfonium ion an uncertainty is introduced by the product, diethyl sulfide, which not only appears in the vapor, but also in a separate liquid phase where it could dissolve some ethylene. For tetraethylammonium hydroxide the rate constants based on ethylene agreed with those based on hydroxide ion within the limits of reproducibility (4%).

Rate of Elimination by *t*-Amyl Chloride. A 0.75 *M* solution of *t*-amyl chloride in 80% methanol was divided into 2-ml. portions for reaction at 29.8° at a variety of pressures and reaction times. The total percentage of reaction was followed by titration of the hydrochloric acid produced, and the total amylene content was followed by titration with bromine. Beyond 50% reaction the ratio of olefin to substitution product began to decline gradually from 0.276 at 1

half-life to 0.210 at 5 half-lives, presumably because of acid-catalyzed addition reactions. Thereafter the reaction mixtures were made 0.5 *M* in sodium acetate, and there was no further difficulty with instability of the products. The constants given in Table II are for the total reaction.

Table II. Summary of Kinetic Measurements

<i>t</i> -Amyl chloride (0.5 <i>M</i>) in 80% ethanol at 34.2°
$k_1^a = 0.162 \text{ hr.}^{-1}$, $k_{240} = 0.205$, $k_{680} = 0.265$, $k_{1020} = 0.345$, $k_{1360} = 0.420$
<i>t</i> -Amyl chloride (0.75 <i>M</i>) in 80% methanol at 29.8°
$k_1 = 0.23 \text{ hr.}^{-1}$, $k_{1360} = 0.56$
<i>t</i> -Amyldimethylsulfonium iodide (0.5 <i>M</i>) in 80% ethanol at 53.8°
$k_1 = 0.52 \text{ hr.}^{-1}$, $k_{1360} = 0.256$
2-Bromobutane (1.0 <i>M</i>) and NaOEt (1.0 <i>M</i>) in ethanol at 47.8°
$k_{20} = 0.232 \text{ l./mole hr.}$, $k_{1360} = 0.381$
<i>t</i> -Amyltrimethylammonium iodide (0.5 <i>M</i>) and KOH (4 <i>M</i>) in ethanol at 84.8°
$k_{34} = 0.039 \text{ l./mole hr.}$, $k_{340} = 0.032$, $k_{680} = 0.027$, $k_{1020} = 0.0218$, $k_{1360} = 0.0194$
Triethylsulfonium bromide (1 <i>M</i>) and NaOH (1 <i>M</i>) in water at 109.0°
$k_{68} \text{ (ethylene)} = 0.139 \text{ l./mole hr.}$, $k_{68} \text{ (ethanol)} = 0.177$, $k_{1360} \text{ (ethylene)} = 0.084$, $k_{1360} \text{ (ethanol)} = 0.128$
Triethylsulfonium bromide (1 <i>M</i>) and NaOCH ₃ (1 <i>M</i>) in methanol at 50.9°
$k_{34} \text{ (total)} = 0.097 \text{ l./mole hr.}$, $k_{1360} = 0.053$
Tetraethylammonium bromide (1 <i>M</i>) and NaOCH ₃ (1 <i>M</i>) in methanol at 104.8°
$k_{68} = 0.107 \text{ l./mole hr.}$, $k_{680} = 0.074$, $k_{1360} = 0.048$

^a The symbol k_p denotes the reaction rate constant at *p* atm.

Rate of Elimination by *t*-Amyldimethylsulfonium Iodide. A solution of 0.5 *M* sulfonium salt and 0.5 *M* sodium acetate in 80% methanol was divided into 2-ml. portions for reaction at 53.8° under ordinary pressure and 1360 atm. The total reaction was followed by titration of the liberated acid as above, but dimethyl sulfide interferes with the determination of olefin by bromine titration. The ratio of olefin to dimethyl sulfide was determined roughly from calibrated gas chromatograms as being 0.67. This figure is probably susceptible to 10% error owing to difficulty in reproducing the calibration, but the ratio of the peak areas of olefin and sulfide in a single chromatogram was reproducible within 2% and did not vary perceptibly with pressure. The reactions were followed to 50% completion for rate measurements, and to 80% for determination of the ratio of Hofmann to Saytzeff product by gas chromatography.

Rate of Elimination by 2-Bromobutane. Samples were prepared by mixing 2 mequiv. of 2-bromobutane (0.22 ml.) with 1.80 ml. of 1.11 *M* sodium ethoxide in absolute ethanol. After a time estimated to give 40–45% reaction the samples were withdrawn and divided into two portions. A 1-ml. portion was used for extraction with carbon tetrachloride to determine the butylenes, and the aqueous layer was combined with the remainder of the reaction mixture for titration of the unreacted alkali. Elimination accounts for 65–67% of the alkali consumed, the remainder being presumed to give substitution.

Rate of Elimination by *t*-Amyltrimethylammonium Iodide. The reaction conditions and results are

(24) H. A. Szymanski, *Anal. Chem.*, **33**, 815 (1961).

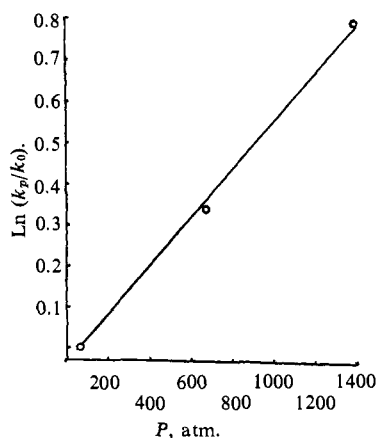


Figure 1. Tetraethylammonium methoxide elimination.

detailed in Table II. The reaction was followed only by bromine titration under the assumption that competition by substitution would not invalidate the relative rates. A reaction mixture from which the base was omitted gave negligible reaction when exposed to the conditions which caused substantial conversion in the presence of base. It is possible that some S_N2 reaction occurs in the presence of base, but this could not be detected by titration of the base under the pseudounimolecular conditions used here. The reactions were followed until 30–40% of the theoretical amylene was produced.

Rate of Elimination by Triethylsulfonium Bromide. Both the aqueous and methanolic reactions were followed by titration of unused base and measurement of the volume of ethylene gas evolved. The analytical procedures are described above, and the kinetic data appear in Table II. Reactions were followed to 30–40% completion.

Rate of Elimination by Tetraethylammonium Bromide. The treatment of this reaction was the same as for triethylsulfonium bromide in methanolic sodium methoxide, except that before titrating unconsumed base it was necessary to add 4–5 ml. of water to a 1-ml. portion of reaction mixture and boil for 1 min. to expel triethylamine.

Typical Determination of Rate Constant. For the elimination by tetraethylammonium ion the appropriate rate equation is

$$dC/dt = -kC^2$$

in which C is the concentration of substrate and also of base (initial value = 1 M). The data in Table III were collected for a pressure of 1360 atm. and a temperature of 104.8°.

Table III

Time, hr.	Vol. of C_2H_4 , ^a ml.	Concn. of base, M	$k_{ethylene}$	k_{base} ^b
5.00	6.90	0.810	0.050	0.047
7.00	8.35	0.758	0.048	0.046

^a The calculated volume of ethylene at completion is 34.6 ml.

^b Units are l./mole hr.

Typical Determination of Volume of Activation. From the data of Table II, values of $\ln(k_p/k_0)$ were computed and plotted against pressure as shown in Figure 1. A graphical determination of the slope gives $\Delta V^*/RT$.

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Mechanisms of Elimination Reactions. VI. The Effect of the Leaving Group on Orientation in E2 Reactions^{1,2}

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When 2-halopentanes are treated with ethoxide ion in refluxing ethanol, the proportion of 1-pentene in the olefinic product increases in the order $I < Br < Cl < F$. When 2-halo-2-methylbutanes are treated with ethoxide ion in refluxing ethanol, the proportion of 2-methyl-1-butene in the olefinic product increases in the order $Br < Cl < F$. In both series, the fluoride shows clearly Hofmann-rule behavior (>70% 1-olefin). 2-Methyl-2-

butyl chloride and bromide give less 2-methyl-1-butene when thiophenoxide is the base than when ethoxide is the base. The bearing of these results on current theories of steric and electronic effects in elimination reactions is discussed.

The tendency of some elimination reactions to give mainly the more substituted olefin (Saytzeff rule) and others to give mainly the less substituted olefin (Hofmann rule) has been explained by Ingold in terms of

(1) This work was supported by the National Science Foundation.
(2) Preliminary account: W. H. Saunders, Jr., S. R. Fahrenholtz, and J. P. Lowe, *Tetrahedron Letters*, No. 18, 1 (1960).