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PYROLYTIC AND BASE-CATALYZED ELIMINATION REACTIONS: EFFECT OF STRUCTURE ON THE RATE OF REACTION

by

Charles Anthony Bishop

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In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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INTRODUCTION

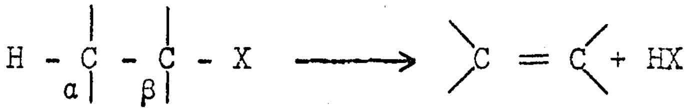
As is often the case in the study of a reaction mechanism, the more work that is done, the more confusing the picture becomes. Such has been the situation in the study of the beta elimination reaction. Although the reaction has been known for over a century, only in recent years has much research been instituted to ascertain the effect of structural changes on the transition state of the reaction. The commonly accepted concept of a preferred *trans* steric course was found to break down with the addition of electron-withdrawing groups to the β-carbon atom. Furthermore, *cis* elimination was observed to dominate over *trans* elimination in systems where a *trans* coplanar transition state could not be attained without setting up excessive strain in the molecule. These observations, and others, are quite naturally closely associated with the structure of the transition state. Two schools of thought have developed in describing the mechanism in terms of the observed results, but this confusing situation is gradually being clarified and an overall picture of the transition state is being developed.

The primary purpose of this thesis is to report a kinetic study of the effect of solvent and base on the elimination reaction of some 2-phenylethyl derivatives. The conclusions drawn from this research are discussed in light of current ideas in an attempt to procure, to some degree, a better understanding of the E2 transition state.

A study of the effect of a variety of leaving groups on olefin distribution and reaction rates in the ester pyrolysis reaction is also reported. A clearer picture of the transition state for this reaction than for the E2 reaction is available. However, only a relatively few esters have been extensively studied and it is difficult to correlate these, for, in general, each ester was studied individually under conditions suitable to that ester. It is hoped that the study of a variety of esters and related leaving groups in a model system will serve to elucidate the factors which determine the course of the reaction and might therefore serve as a basis for future research in this field.

HISTORICAL

Unsaturation is generally introduced into an organic molecule by the loss of two substituents from a pair of adjacent bound carbon atoms in a chain or ring. In the most general case, a proton is lost from one carbon atom, designated the β-carbon atom, and a nucleophile, X, is lost from the other, or α-carbon atom. This so-called "beta elimination" comprises the breaking of two σ bonds to form a new π bond between the carbon atoms.



(Eqn. 1)

The beta elimination reaction has been widely studied not only for its synthetic utility but because of its theoretical interest. Much of the theory regarding the mechanism of the reaction has been correlated on the basis of kinetic evidence and polar effects by the Hughes and Ingold school.[1] They have suggested a general kinetic theory involving a unimolecular elimination, the E1 reaction, and a bimolecular elimination, the E2 reaction. The E1 reaction (Eqn. 2) involves a rate determining ionization to a carbonium ion followed by a rapid loss of a proton to form an olefin. The

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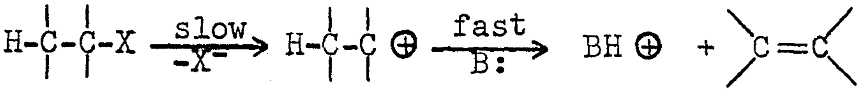
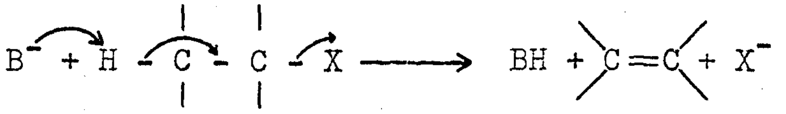
[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press. Ithaca, N.Y., Chapter 8, p. 420 (1953).

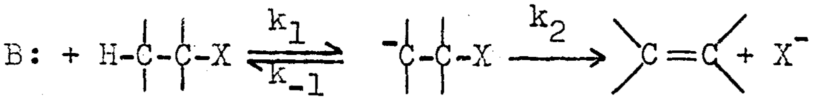
E2 reaction (Eqn. 3), because of its observed stereochemistry,


(Eqn. 2)

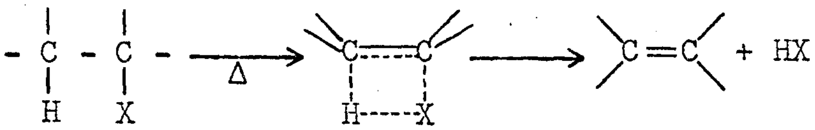
was considered to involve a trans coplanar transition state in which the formation of olefin and the loss of proton and leaving group occurred simultaneously under the influence of


(Eqn. 3)

base. A special case of the E2 reaction involving elimination from a carbanion formed in a prior rate determining equilibrium was also suggested.[1] This is known as the ElcB mechanism (Eqn. 4).


(Eqn. 4)

A third type of elimination, the pyrolytic elimination reaction, is a thermally induced, unimolecular decomposition of an ester to give as products an acid and olefins (Eqn. 5).


(Eqn. 5)

The position of the double bond in unsymmetrical elimination reactions can generally be predicted on the basis of the Hofmann[2] and Saytzeff[3] rules. The Hofmann rule states, "In the elimination of onium ions ($-NR_3^+$, $-SR_2^+$, $-PR_3^+$) the predominating product is the olefin that has the least number of alkyl groups attached to the double bond." Hughes, Ingold and coworkers[1] interpreted this rule on the basis of polar effects. In their view, the strong inductive effect of the positively charged onium ion is responsible for acidifying the β-proton thus making this effect dominant. For example, in the elimination of n-propylethyldimethylammonium hydroxide with base, the protons on both the ethyl and n-propyl groups are acidified by the inductive effect of the positively charged nitrogen atom. But this effect is partially offset in the n-propyl group by the electron-releasing effect of the adjacent methyl group. Thus, ethylene is the predominant olefinic product formed by elimination involving the most acidic proton. In contrast, the Saytzeff rule states, "In the dehydrohalogenation of secondary and tertiary halides, the most highly substituted ethylene is the predominating product." Here the halogen atom is believed to be less effective than a positively charged atom in acidifying the β-hydrogens, so that instead of proton acidity, the stability of the olefinic product forming becomes the rate determining factor.

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[2] A. W. Hofmann, Ann., 79, 11 (1851).

[3] A. Saytzeff, ibid., 179, 296 (1875).

Brown and coworkers have suggested that steric effects play a dominant role, and indeed, are probably the underlying rate determining factors in the balance between Hofmann and Saytzeff elimination.[4] This view has been challenged by Saunders in a recent article, where it is shown that the nature of the halide leaving group in base catalyzed elimination reactions has a profound effect on olefin distribution.[5] Furthermore, the results of this study are in the opposite direction for those expected for a steric effect. In their latest publication, Hughes and Ingold have reiterated their belief that polar effects determine the balance between Hofmann and Saytzeff elimination with steric control dominating only in extremely hindered cases.[6]

The pyrolytic elimination reaction, especially of acetates, amine oxides, and xanthates has been widely studied. Olefin distribution data have been explained on the basis of steric, electronic and statistical effects.[7, 8] On the basis of the unimolecular, *cis* steric course of the reaction, the

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[4] H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, *78*, 2190 (1956) *et seq.*, and papers cited therein.

[5] W. H. Saunders, Jr., S. R. Fahrenholtz and J. P. Lowe, *Tetrahedron Letters*, *No. 18*, 1 (1960).

[6] B. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960).

[7] D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *J. Am. Chem. Soc.*, *81*, 643 (1959).

[8] C. H. DePuy and R. W. King, *Chem. Rev.*, *60*, 431 (1960).

mechanism is generally considered to involve a cyclic concerted transition state.[7, 8] Attempts to elucidate the direction of elimination of acetates[7] and amine oxides[9] have been carried out recently, but almost no information is available about directional effects of other leaving groups. Furthermore, little quantitative data are available on the rates of pyrolysis of other leaving groups. The effect of the strength of the eliminated acid was investigated by Bailey and Hewitt,[10] who found that the reaction was faster for esters of stronger acids. Smith and Wetzel also noted a correlation between acid strength and pyrolysis temperature in the elimination of some cyclohexyl esters.[11] No quantitative data are available, however, on just how much the rate of pyrolysis is increased. Amides have been found to be much less reactive than acetates, requiring pyrolysis temperatures some 100°C. higher than the corresponding ester.[12, 13] Vinyl ethers decompose thermally at about the same rate as acetates

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[9] A. C. Cope, N. A. LeBel, N. H. Lee and W. R. Moore, J. Am. Chem. Soc., 79, 4720 (1957).

[10] W. J. Bailey and J. J. Hewitt, J. Org. Chem., 21, 543 (1956).

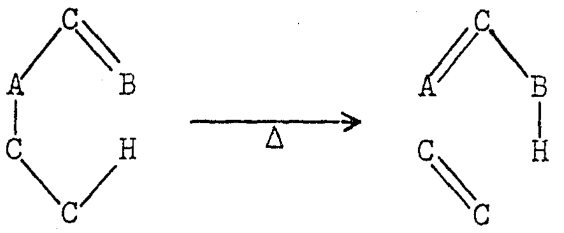
[11] G. G. Smith and W. H. Wetzel, J. Am. Chem. Soc., 78, 875 (1957).

[12] W. J. Bailey and C. N. Bird, J. Org. Chem., 23, 996 (1958).

[13] H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, J. Am. Chem. Soc., 80, 4588 (1958).

to yield olefins and acetaldehyde.[14] It has also been noted that sec-butyl benzanilimidate underwent thermal cracking to give 2-butene and benzanilide as products.[15] Each of these classes of compounds was, in general, studied individually and little data are available for comparison of one with another.

Consideration of the general type of compound which undergoes pyrolysis (Eqn. 6) in which the atoms A and B are varied suggests the possibility of a correlation between leaving group and ease and direction of elimination.



(Eqn. 6)

Prior to 1950, the preferred trans steric course of the E2 reaction had been demonstrated in a great number of systems and evidence had accumulated that the transition state of the reaction possesses enough double bond character to seriously effect rate and product balance.[16] These facts together with

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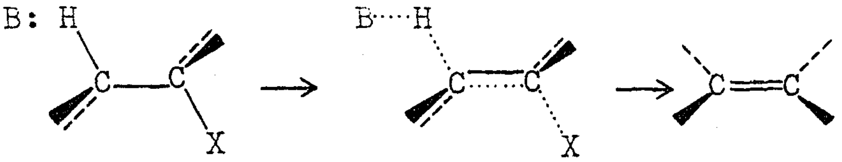
[14] A. T. Blades and G. W. Murphy, ibid., 74, 1039 (1952).

[15] K. B. Wiberg and B. I. Rowland, ibid., 77, 2206 (1955).

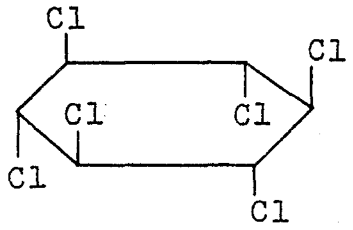
[16] D. J. Cram, "Olefin Forming Elimination Reactions", In M. S. Newman, ed., "Steric Effects in Organic Chemistry", John Wiley and Sons, Inc., New York, N.Y., p. 305 (1956).

the observed second order kinetics of the E2 reaction led to a commonly accepted idea of a transition state in which the four centers (H-C-C-X) involved were coplanar and with the proton and leaving group being lost simultaneously from opposite sides of the molecule (Eqn. 7).



(Eqn. 7)

In recent years, studies of base promoted elimination reactions have indicated the need of revision of these commonly accepted ideas. Evidence has accumulated for the dual nature of the transition state in systems where the β-proton is activated by the presence of electron-withdrawing groups or where the proton and leaving group cannot become trans and coplanar in the transition state. Evidence has been presented that in such systems, the transition state may take on a large amount of carbanionic character, becoming more like the E1cB transition state. In fact, there is evidence that in some extreme cases, the reaction may involve two stages with a carbanion intermediate. One of the first indications of a carbanion mechanism in the elimination reaction was the observation by Cristol and coworkers that the β-isomer of benzene hexachloride (I) underwent base catalyzed elimination at a rate which was 7,000 to 24,000 times slower than any of the other isomers.[17, 18]



I

The chlorine atoms in the β-isomer are all _trans_ to one another making the possibility of a coplanar transition state unlikely because of the extreme strain developed in the molecule in attaining such a structure. The very slow reaction of this isomer is good evidence for the energetic preference for _trans_ over _cis_ elimination and lends support to the theories concerning the stereochemistry of the reaction. Yet the fact that _cis_ elimination went at all and still showed good second order kinetics was surprising. Two mechanisms might explain the observed results; a concerted _cis_ elimination of hydrogen and chlorine from the molecule (with the simultaneous formation of a double bond), and a two stage E1cB reaction involving a carbanion intermediate.

Cristol tested the idea of a carbanion intermediate[18, 19]

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[17] S. J. Cristol, _J. Am. Chem. Soc._, _69_, 340 (1947).

[18] S. J. Cristol, N. L. Hause and J. S. Meek, _ibid._, _73_, 674 (1951).

[19] S. J. Cristol and D. D. Fix, _ibid._, _75_, 2647 (1953).

by conducting the above reaction in deuterated solvent for one-half lifetime and observed that the recovered β-isomer contained a very small amount of deuterium. This was taken as evidence for the E1cB mechanism in the reaction of this isomer. It was pointed out, however, that the reaction of the carbanion intermediate to give products (k_2) had to be 150 times as fast as the reverse reaction to give reactants (k_{-1}) in order to account for the observed results.

Later, Cristol and coworkers showed that the marked preference for _trans_ over _cis_ elimination could be greatly reduced in systems in which the four centers H-C-C-X could not achieve _trans_ coplanarity.[20, 21]

The flexibility of the cyclohexane ring may be considerably diminished by incorporating it into a bicyclic system. It was observed that _cis_ elimination (from the _trans_ substrate) was preferred over _trans_ elimination (from the _cis_ substrate) in the second order base catalyzed elimination of 11,12-dichloro-9,10-dihydro-9,10 -ethanoanthracene (II).[20] This same result was observed in the elimination of 2,3-dichloronorbornane, the endo _cis_ isomer (III) reacting slower than the isomer with the chlorine atoms _trans_ to one another.[21] In both these systems the overall rate of

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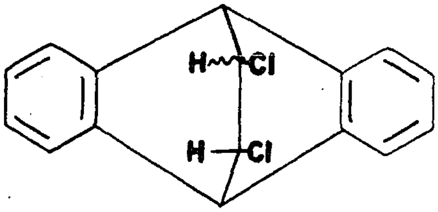
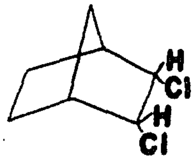
[20] S. J. Cristol and N. L. Hause, _ibid._, _74_, 2193 (1952).

[21] S. J. Cristol and E. F. Hoegger, _ibid._, _79_, 3438 (1957).

elimination was very slow. These observations led to the conclusion that the bimolecular elimination is not selective in systems which cannot attain a trans coplanar transition state. This non-selectivity probably means that these systems either react via an ElcB mechanism or by a concerted cis elimination.



II



III

It is reasonable that the ElcB mechanism with its carbanion intermediate should be more sensitive than a concerted reaction to changes in the acidity of the β-proton. This point was investigated further by Cristol and coworkers.[21, 22, 23] They showed that when the strongly acid-strengthening p-tolylsulfonyl group was incorporated into molecules II and III instead of one of the chlorine atoms, converting them to β-chlorosulfones, the base catalyzed elimination of hydrochloric acid from the molecule occurred many times faster (about 10^{10} times) than in the original

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[22] S. J. Cristol and R. P. Arganbright, ibid., 79, 3441 (1957).

[23] S. J. Cristol and N. P. Norris, ibid., 76, 3005 (1954).

compounds. Bordwell also observed rate enhancement from the substitution of the p-tolylsulfonyl group in the β-position (*vide infra*). In these systems, then, where a *trans* coplanar transition state was unattainable, acid strengthening groups attached to the β-carbon did facilitate elimination strongly, suggesting either the presence of a carbanion intermediate or at least considerable carbanionic character at the β-carbon in the transition state. Indeed, it has been found that sufficient acidification of the β-proton can bring about *cis* elimination even when *trans* elimination is structurally possible. Bordwell has shown that *trans*-2-tolylsulfonylcyclohexyl tosylate reacts with base to form 1-*p*-tolylsulfonylcyclohexene with the double bond adjacent to the sulfone group rather than 3-*p*-tolylsulfonylcyclohexene, the product expected from *trans* elimination.[24] The "detosylation" of *trans*-2-*p*-tolylsulfonylcyclopentyl tosylate proceeds in the same manner.[25] Moreover, when the rates of elimination of the above *trans* compounds are compared with the *cis* compounds, a great reduction in the preference of *trans* over *cis* elimination was observed. In fact, when triethyl amine was used as base, *trans* elimination proceeded at almost the same rate as *cis* elimination in one case.

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[24] F. G. Bordwell, *et al.*, *ibid.*, *77*, 1141, 1145, 6706 (1955).

[25] J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, *78*, 3468 (1956).

The diminished preference of trans over cis elimination in these systems can be attributed either to the inability of the proton and leaving group to attain an energetically favorable trans coplanar position in the transition state or to the fact that the acidity of the β-proton is so great that it is lost in the rate determining step with little double bond formation. In either case, the differences in energy of activation between cis and trans elimination would be expected to be minimized.

Another instance where the rates of cis and trans elimination were observed to be very nearly the same was reported by Goering and coworkers.[26] They observed that in the base catalyzed elimination reactions of cis and trans 2-p-tolylsulfonylcyclohexyl and 2-p-tolylsulfonylcyclopentyl chlorides, trans elimination was favored over cis elimination by factors of 490 and 35 respectively. This system was the same one used by Bordwell for his tosylate eliminations; and when the results were compared, it was found that, contrary to expectations, the rates of elimination of trans-2-p-tolylsulfonycyclohexyl chloride and trans-2-p-tolylsulfonylcyclohexyl tosylate were virtually the same. Goering explained this in the following way. Cyclohexyl tosylate[27] has been found to be 180 times as reactive as cyclohexyl

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[26] H. L. Goering, D. I. Relyea and K. L. Howe, ibid., 79, 2502 (1957).

[27] S. Winstein and N. J. Holmes, ibid., 5562 (1955).

chloride[28] under similar conditions (and presumably both reacting by a concerted E2 mechanism) and 10^6 times less reactive than the sulfones in question. It seems unlikely that a sulfone group could accelerate a concerted trans elimination at C_3 or an Sn_2 displacement at C_2 by a factor of 10^6, for a strongly electron-withdrawing group at C_1 would be expected to retard these processes. The expected product was, therefore, 1-p-tolylsulfonylcyclohexene. If the reaction was concerted, the tolylsulfonylcyclohexyl chloride should have reacted by two powers of ten slower than the corresponding tosylate. The fact that it did not is consistent with the ElcB mechanism in which a carbanion is formed in a rate determining step followed by a rapid reaction to give products. In this event, the reactivity of the leaving group would be of no consequence since it is reacting in a fast step.

What was not noted in this work, however, was the fact that the base catalyzed elimination reactions of the cis-2-p-tolylsulfonylcyclohexyl chloride and tosylate also take place at the same rate. These two compounds can presumably undergo E2 elimination, since models show that it should not be difficult for the leaving group to become trans and coplanar with the β-proton. It is unlikely that these two species

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[28] E. D. Hughes, C. K. Ingold and J. B. Rose, J. Chem. Soc. 3839 (1953).

would undergo reaction to give a carbanion intermediate when the energetically favorable E2 path is available (vide infra). In light of this observation, Goering's explanation would seem to be considerably weakened, for it calls for an ElcB mechanism on the basis of identical rates of the trans chloride and tosylate when, in fact, the cis compounds also have nearly identical rates. On these grounds, a better explanation might be that both series undergo a concerted elimination, one by a cis path and the other trans.

Very recently, Cristol and Stermitz reported a study of the products and rates of elimination of the cis and trans isomers of 2-phenylcyclohexyltrimethylammonium ion and 2-phenylcyclohexyldimethylsulfonium ion in ethanolic potassium hydroxide.[29] The cis-sulfonium salt underwent elimination at the same rate as its acyclic 2-phenylethyl analog. In contrast, the cis-ammonium salt reacted 80 times slower than its acyclic analog. Both these reactions are believed to involve a trans coplanar transition state with the ammonium salt reacting slower because of conformational difficulties. On the other hand, the trans compounds reacted slower than the cis compounds by factors of 133 for the ammonium salt and 383 for the sulfonium salt. These results were interpreted in terms of a multistage elimination process for those compounds

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[29] S. J. Cristol and F. R. Stermitz, J. Am. Chem. Soc., 82, 4692 (1960).

that were forced to undergo cis elimination.

The evidence cited thus far supports the view that a carbanion intermediate can exist in the beta elimination reaction in special cases where a planar four centered transition state is unattainable or where the β-proton is especially acidified. Nevertheless, the ElcB mechanism was never unambiguously established by any of this research.

Evidence against an ElcB mechanism is based on deuterium exchange studies and on studies of general and specific base catalysis in the systems in question.

Bordwell, in further work on the elimination reaction of cis and trans p-tolylsulfonylcyclohexyl and p-tolylsulfonylcyclopentyl tosylate, observed the reaction to be general base catalyzed.[30] In his view, if the ElcB mechanism was operative here, the rate of reaction would be a function of the concentration of the anion, $^{-}C\text{-}C\text{-}X$, and this anion concentration in turn a function of the concentration of base, B, and its

$$B{:} + HOH \rightleftharpoons BH^{+} + {}^{-}OH \qquad \text{(Eqn. 8)}$$

conjugate acid BH^{+}. In aqueous solution, the rate would therefore depend only upon the hydroxide ion concentration, and specific base catalysis would be observed. However, if

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[30] J. Weinstock, R. G. Pearson and F. G. Bordwell, ibid., 78, 3473 (1956).

general base catalysis was observed, which is the case, then the reaction must either be concerted or be a rate controlling ionization followed by a rapid reaction of the anion. He calculated that the carbanion, if formed, could only have a lifetime of 10^{-9} seconds.

The lack of deuterium exchange in the reacting molecule is held by many as evidence for the absence of a carbanion intermediate in the elimination reaction. Skell and Hauser[31] observed that no deuterium exchange took place in the β-position in the base catalyzed elimination of 2-phenylethyl bromide in deuterated alcohol. A carbanion, if formed, should not only react to give products but should undergo a reverse reaction with solvent to give starting material according to the E1cB mechanism. Cristol's observation that the β-isomer of benzene hexachloride underwent deuterium exchange was not considered strong evidence, in view of the very small amount ($<$ 1%) of deuterium exchange observed. These views, in fact, supported the theory of Hughes and Ingold, who after extensive work on elimination reactions, postulated that, in elimination reactions of alkyl halides to form olefins, the β-proton and halide ion are removed simultaneously.[32]

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[31] P. S. Skell and C. R. Hauser, ibid., 67, 1661 (1945).

[32] E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, J. Chem. Soc., 899 (1940).

It must be remembered that, although the β-proton of 2-phenylethyl bromide is acidified by the phenyl ring, rotation about the C_α-C_β bond is not restricted, so that a trans coplanar transition state can be attained. Therefore, this result cannot be applied to strained systems and the absence of deuterium exchange in the 2-phenylethyl system does not completely disprove the presence of a carbanion intermediate in strained systems.

In a further comparison of strained with "normal" systems, Skell and McNamara found that the two diasteriomeric 2-benzenesulfonyl-3-iodobutanes, upon reaction with pyridine, each gave a different 2-benzenesulfonyl-2-butene.[33] In comparing this result with Bordwell's work[24] on the reaction of a similar compound, Skell states, "In elimination reactions where no overpowering restrictions preclude trans elimination, the separation of H and X from the parent molecule occurs simultaneously, even in those cases where the hydrogen is activated by a powerful electron-withdrawing group." Support for this observation is found in other open chain systems which have activated protons.[34] It was pointed out, however, that sufficient activation of the proton by electron withdrawing groups, even in alicyclic systems, could result

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[33] P. S. Skell and J. H. McNamara, J. Am. Chem. Soc., 79, 85 (1957).

[34] F. G. Bordwell and P. S. Landis, ibid., 79, 1593 (1957).

in an E1cB mechanism.[31]

The absence of a distinct carbanion in the beta elimination reaction, as shown by the absence of deuterium exchange with the substrate and by general base catalysis, points to a transition state with sizable double bond character for cis as well as trans elimination. Of course, this is based on the reasonable assumption that a carbanion, if formed, would undergo reaction to products (k_2) and reverse reaction to reactants (k_{-1}) at comparable rates. Cristol,[21] however, points out that the E2 mechanism is not distinguishable from the E1cB mechanism by deuterium exchange studies or by studies of general base catalysis when $k_2 \gg k_{-1}$, but will only be distinguishable when the sensitivities of the methods available for analysis of such results are consistent with the ratio k_{-1}/k_2. It thereby is implied that, if a carbanion intermediate is formed, in most cases encountered it has no choice but to react to form products. It seems unlikely, in all systems studied thusfar, that k_{-1} should be so much slower than k_2. It may be that when sufficient strain is imposed on the molecule or when the β-protons are extremely acidified so that the reaction is shifted to the E1cB type, the kinetics are such that $k_2 \gg k_{-1}$. On the other hand, the first step of the E1cB mechanism might not be an equilibrium at all, but a rate determining irreversible ionization to a carbanion.

Indeed it is reasonable to expect the E1cB and E2 mechanisms to merge into each other as the lifetime of the ElcB carbanion becomes progressively shorter. The criterion for an ElcB mechanism, such as specific hydronium ion catalysis in aqueous solution, reaction of the carbanion intermediate with deuterated solvent to give deuterated starting material, and lack of stereospecificity, should be lost at different stages.[35] Starting from the ElcB end of the scale, the first criterion to be lost should be the ability of the starting material to exchange deuterium with solvent via a true carbanion intermediate. Somewhat further along the reaction should show a <u>trans</u> stereochemical preference, which is an important criterion for a true E2 reaction. This argument implies the existence of a transition state for the E2 reaction which has various degrees of carbanionic character and double bond character. Recent studies have shown this to be the case for most elimination reactions. Research designed to determine changes in carbon-hydrogen bond breaking relative to carbon-leaving group bond breaking with changes in solvent, base and leaving group, isotope effect studies, and determination of Hammett ρ-values have all contributed to a better understanding of structural and environmental effects on the transition state of the reaction.

In an effort to elucidate the dual nature of the E2

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[35] V. J. Shiner, Jr. and M. L. Smith, ibid., 80, 4095 (1958).

transition state, Cram, Greene and DePuy investigated eclipsing effects in the base catalyzed elimination of *erythro* and *threo* 1,2-diphenyl-1-propyl bromides, iodides and ammonium salts with changes in solvent and base.[36] Applying the Hammond postulate,[37] they described the transition state of the reaction as being more like products in some cases (and therefore closer to the E2 mechanism), and more like reactants in others (closer to the E1 or E1cB mechanism). Since the ground state energies of the *erythro* and *threo* compounds are about the same, one would expect the diasteriomers to have about the same rates if the transition states were like reactants. On the other hand, with the equilibrium ratio of *trans* to *cis* olefin being about 50, one might expect quite different rates if the transition state were like products. As with olefinic products, eclipsing effects are the only difference between the two diasteriomeric transition states. The results were best explained by invoking three possible transition state structures, IV, V and VI, which are the transition states for the E1, E2 and E1cB reactions, respectively. HOS represents the solvent and B^- the base.

When the 1,2-diphenyl-1-propyl bromides and iodides were reacted with sodium ethoxide in ethanol, the relative rate

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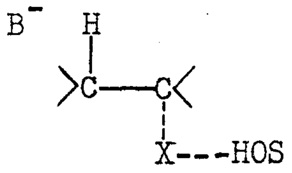
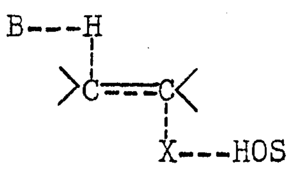
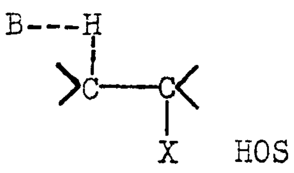
[36] D. J. Cram, F. D. Greene and C. H. DePuy, *ibid.*, *78*, 790 (1956).

[37] G. S. Hammond, *ibid.*, *77*, 334 (1955).


IV


V


VI

threo/erythro in each case was about one, showing that the transition state is probably closer to structure IV with carbon-halogen bond breaking being more important than carbon-hydrogen bond breaking. When the same solvent-base system was used with a trimethylammonium salt as the leaving group, the ratio was 57, showing that in this case the transition state had been shifted so it looked more like products (structure V). When the bromides and iodides were reacted in the stronger base t-butoxide and the poorer solvating medium, t-butanol, the carbon-hydrogen bond becomes more easily broken relative to the carbon-halogen bond and, as expected, the rate ratio threo/erythro is 5.4 for the bromides and 15 for the iodides. The transition state in these cases is shifted toward structure V. When the ammonium salt was reacted in the t-butoxide-t-butanol system, the relative rate dropped to almost one, the explanation here being that the transition state is shifted toward structure VI because carbon-hydrogen bond breaking becomes more important than carbon-nitrogen bond breaking in the stronger base and poorer solvating medium. For the halides, in general, the stronger base gave rise to a transition state with more double bond character and hence greater eclipsing of adjacent groups.

The close coupling of carbon-hydrogen and carbon-leaving group bond breaking and the effect on this of base strength and solvent was thus exhibited. More importantly, the dual nature of the transition state and the ability to shift it from more or less carbanionic character was demonstrated. Obviously, a relative idea of the localization of charge in the transition state for various leaving groups and under various conditions was needed at this point.

A relative measure of the charge generated on the β-carbon atom in the transition state of the E2 reaction can be secured from a Hammett[38] study of 2-aryl substituted compounds. In the 2-phenylethyl system, for example, the overall effect of a phenyl ring in the β-position is acidification of the β-protons by an inductive effect. Nevertheless, by proper substitution on the phenyl ring, the electronic character around the β-carbon atom can be changed so that a relative measure of the charge built up on the β-carbon atom in the transition state can be obtained for different compounds under various conditions. The Hammett ρ-value is an evaluation of the sensitivity of the reaction to these substituents,[38, 39]

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[38] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York, N.Y., p. 184 (1940).

[39] H. H. Jaffe, Chem. Rev., 53, 191 (1953).

measuring the difference in electron density between the ground state and the transition state at the β-carbon atom. A large positive ρ-value indicates the development of a large amount of negative charge at the β-carbon in the transition state.

Cristol and coworkers studied substituent effects for the elimination of 2,2-diphenyl-1,1-dichloro and 2,2-diphenyl-1,1,1-trichloroethane[40] in ethanolic sodium hydroxide and found the reaction to be very sensitive to the presence of acidifying groups in the benzene ring, ρ for the reaction being +2.456 and +2.729, respectively. Simonetta and Favini showed that the value for the reaction of 2-phenylethyl chloride with hydroxide ion in aqueous alcohol solution was +1.65, although through a miscalculation they reported it to be +0.0165.[41] For chlorides, at least, the β-carbon atom has some degree of negative character in the transition state.

Substituent effects in the bimolecular elimination reaction of a variety of 2-phenylethyl compounds in ethanol using ethoxide as base were studied by DePuy and Froemsdorf,[42]

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[40] S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eilar and J. S. Meek, J. Am. Chem. Soc., **74**, 3333 (1952).

[41] M. Simonetta and G. Favini, J. Chem. Soc., 1840 (1954).

[42] C. H. DePuy and D. H. Froemsdorf, J. Am. Chem. Soc., **79**, 3710 (1957).

and by Saunders and Williams.[43] The results showed that a great deal of carbanionic character was developed in the transition state of the reaction. Thus, for a series of *m*- and *p*-substituted 2-phenylethyl bromides and iodides the Hammett ρ-values were +2.1. This value was +2.3 when tosylate was the leaving group and rose to +2.7 for the corresponding sulfonium bromide. On the other hand, it was recognized that a certain amount of double bond character was present in the transition state, for the sensitivity of the rate of elimination to the nature of the leaving group showed carbon-hydrogen and carbon-leaving group bond breaking are highly synchronous.

The rather high ρ-value for the bromides and iodides in the 2-phenylethyl system is rather surprising in view of Cram's results,[36] where he found that his data on the elimination reaction of 1,2-diphenyl-1-propyl bromides and iodides in ethanol and ethoxide could best be explained by invoking an E1 type transition state (*vide supra*). DePuy's results could better be explained on the basis of structures V and VI. Apparently, an α-phenyl group has the opposite effect from that observed for a β-phenyl group, although Cram's system also contained a β-phenyl group.

DePuy's and Saunders' work encompassed both "Saytzeff"

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[43] W. H. Saunders, Jr. and R. A. Williams, *ibid.*, *79*, 3712 (1957).

leaving groups, i.e., bromides, iodides and tosylates (uncharged leaving groups) and a "Hofmann" leaving group, i.e. dimethylsulfonium bromide (charged leaving group). In all of these, however, the acidity of the β-proton was the rate determining factor, which is suggested to be characteristic of a Hofmann elimination. 2-phenyl-1-bromopropane reacts more slowly than 2-phenylethyl bromide in the elimination reaction.[35] Thus, a β-methyl substituent slows the reaction which is characteristic of a Hofmann-type elimination, but differs from ordinary Saytzeff elimination of alkyl halides where a β-methyl substituent would have an accelerating effect on the rate of reaction. Moreover, the sulfonium salt, which ordinarily follows the Hofmann rule, was more sensitive to electrostatic effects than the halides, which ordinarily undergo Saytzeff elimination. It seems clear that two factors may contribute to the acidity of the β-proton, viz., the inductive effect of the substituent of the β-carbon atom and the inductive effect of the leaving group.

Additional studies on the character of the transition state in the elimination reaction of 2-phenylethyldimethylsulfonium salts were carried out by Saunders and coworkers. The sulfur isotope effect in the reaction of 2-phenylethyldimethylsulfonium bromide with sodium hydroxide in aqueous solution was found to be very small, i.e., little carbon sulfur bond breaking takes place in the transition state of the reaction.[44] These data, taken together with the sizable negative charge generated on the β-carbon atom in the transition state (ρ=2.7),[42, 43] suggest that the nature of the transition state could best be described as being close to structure VI, i.e., close to an ElcB mechanism involving a carbanion. Despite the carbanionic character of the transition state, this sulfonium salt did not exchange deuterium at the β-position during the reaction in deuterated solvent,[45] indicating either the absence of a discreet carbanion intermediate or else that the carbanion intermediate if formed reacted to give products exclusively. At the same time, the deuterium isotope effect at the β-carbon atom was determined using 2,2-dideutero, 2-phenylethyl compounds for comparison. The sulfonium salt showed a sizable isotope effect, k_H/k_D being 5.1 at 30°C.[45] This is not the maximum isotope effect for complete carbon-hydrogen bond breaking at this temperature, but does show a considerable amount of carbon-hydrogen bond breaking in the transition state. These facts indicate that at least some double bond character exists in the transition state and speak against a discreet carbanion intermediate.

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[44] W. H. Saunders, Jr. and S. Asperger, <u>ibid.</u>, <u>79</u>, 1612 (1957).

[45] W. H. Saunders, Jr. and D. H. Edison, <u>ibid.</u>, <u>82</u>, 138 (1960).

Some current work is being done on 2-phenylethyltrimethylammonium salts. It might be expected that the behavior of these compounds would be similar to the sulfonium salts in this system. Indeed, 2-p-nitrophenylethyltrimethylammonium iodide substituted with tritium in the β-position has been found not to undergo proton exchange in the β-position in the elimination reaction with base to give p-nitrostyrene.[46] A tritium isotope effect was observed in this system showing that the β-carbon-hydrogen bond is being broken in the transition state. Saunders, et al., confirmed this by determining the deuterium isotope effect for 2-phenylethyltrimethylammonium bromide, finding k_H/k_D equal to 3.4 at 30°C.[45] Preliminary results indicate that this system has a ρ-value of about +4 in ethanol and ethoxide, the largest value observed for any leaving group in this system and showing a large amount of carbanionic character at the β-carbon atom in the transition state.[47] However, it should be noted that this ammonium salt shows a sizable nitrogen isotope effect, contrary to expectations, for if indeed the ammonium salt does have a higher ρ-value than the sulfonium salt, it should show a smaller amount of carbon-nitrogen bond breaking in the

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[46] E. M. Hodnett and J. J. Flynn, Jr., ibid., 79, 2300 (1957).

[47] C. H. DePuy. "Electronic Effects in Elimination Reactions", [To be published in J. Am. Chem. Soc. circa. 1961].

transition state.[48] Apparently, these two leaving groups are different in their reaction characteristics and definite data should be available before any firm conclusions about this difference can be drawn.

Saunders also measured the deuterium isotope effect in the elimination of 2,2-dideutero-2-phenylethyl bromides, iodides and tosylates in both ethoxide in ethanol and _t_-butoxide in _t_-butanol.[45] The results of this study will be discussed in the next section.

The rate of elimination of 2-phenylethyl tosylate in ethoxide and ethanol was somewhat surprising. The relative rate tosylate: iodide: bromide in this reaction was 1:68:11. At the same time the tosylate group was more reactive than the bromides or iodides in the displacement reaction with ethoxide ion.[42] Moreover, the rate ratio tosylate: iodide: bromide in solvolytic reactions is about 20:2:1.[49] Further investigation of this sluggishness of tosylate elimination is reported in this thesis.

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[48] E. Buncel and A. N. Bourns, _Can. J. Chem._, _38_, 2457 (1960).

[49] A. Streitweiser, _Chem. Rev._, _56_, 602 (1956).

RESULTS AND DISCUSSION

The p-toluenesulfonate group (hereafter referred to as tosylate group) has been shown to be less reactive than even bromide in the elimination reaction in the 2-phenylethyl system.[50] In this system, however, the β-protons are acidified by the inductive effect of the β-phenyl group. To show the reactivity of the tosylate group relative to bromides and iodides in simple, unactivated systems, a series of aliphatic tosylates was prepared and reacted in turn with ethoxide ion in ethanol and with iodide ion in dry acetone. The observed rates of reaction were compared with literature values for the corresponding bromides and iodides. Pertinent data are recorded in Tables 1 and 2. Rate constants for the reactions of iodide were measured by the adsorption indicator technique,[51] and those for the reaction with ethoxide by titration with acid. Olefin yields were determined bromometrically and checked where possible by spectra or gas phase chromatography. All rates were clearly second order.

Examination of the data clearly shows that tosylates react in displacement and elimination at a rate which is often slower than the corresponding bromides and much slower than

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[50] C. H. DePuy and D. H. Froemsdorf, J. Am. Chem. Soc., 79, 3710 (1957).

[51] H. Diehl and G. F. Smith, "Quantitative Analysis", John Wiley and Sons, Inc., New York, N.Y., p. 335 (1952).

Table 1. Rates of reaction of some simple bromides, iodides and tosylates with iodide ion in acetone at 40°C.

Compound	Rate	k_{Br}/k_{OTos}	Ref.
$MeCH_2CH_2Br$	7.3×10^{-3}		52
$MeCH_2CH_2OTos$	1.3×10^{-3}	5.4	
$Me_2CH\ I$	290×10^{-5}		53[a]
$Me_2CH\ Br$	6.9×10^{-5}		52
$Me_2CH\ OTos$	9.4×10^{-5}	0.73	
$Me_2CH\ CH_2Br$	3.4×10^{-4}		52
$Me_2CH\ CH_2OTos$	0.8×10^{-4}	4	

[a] Extrapolated from values at lower temperatures.

Table 2. Rates of reaction of some bromides, iodides and tosylates in sodium ethoxide-ethanol solution

Compound	T. (°C.)	$k \times 10^4$ (l./mole-sec.)	$\frac{k_{Br}}{k_{OTos}}$	%E2	Ref.
$Me_2CH\ CH_2Br$	55	1.4		60	54
$Me_2CH\ CH_2OTos$	55	1.8	0.77	44	
$C_6H_5CH_2CH_2I$	30	26		~100	50
$C_6H_5CH_2CH_2Br$	30	4.1		96	50
$C_6H_5CH_2CH_2OTos$	30	1.2	3.7	33	50
$MeCH_2CH_2Br$	40	1.26	0.3	9	54
$MeCH_2CH_2OTos$	40	4.58		small	

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[52] L. Fowden, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 3187 (1955).

[53] P. B. D. de la Mare, *ibid.*, 3196 (1955).

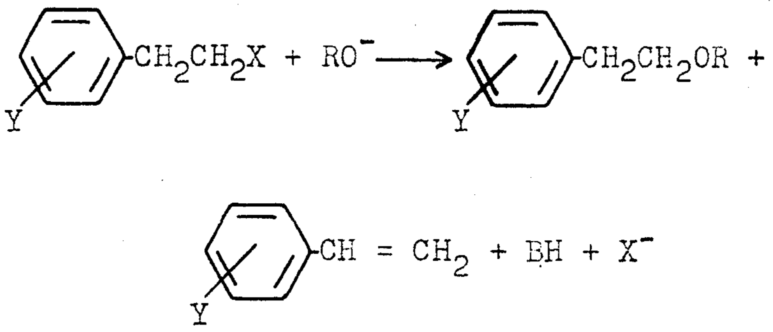
[54] M. L. Dhar, E. D. Hughes, C. K. Ingold and S. Masterson, *ibid.*, 2055 (1948).

the iodides. This result is strikingly different from that observed in solvolytic reactions, where the rate ratio, tosylate: iodide: bromide is 20:2:1. Thus, the apparently abnormally slow rate of elimination of the tosylate group in the 2-phenylethyl system is not peculiar to that system alone, but also appears in very simple systems where the β-protons are not especially activated. Reasons for this behavior will be discussed in light of the results observed in other systems (vide infra).

In an attempt to depict more precisely the transition state of the E2 reaction in the 2-phenylethyl system, and especially to secure a better idea of the timing of the bond-breaking processes, a study of the rates of the E2 reaction of substituted 2-phenylethyl bromides, iodides and tosylates with potassium t-butoxide in t butyl alcohol and with potassium ethoxide in t-butyl alcohol was undertaken. The rates of these same 2-phenylethyl derivatives had previously been measured in sodium ethoxide in ethanol so that a basis for comparison was established.[50] It was hoped that a study of substituent effects with the stronger base, potassium t-butoxide would lead to a better understanding of the removal of the β-hydrogen atom, and at the same time, elucidate the reasons for the abnormally slow rate of elimination of tosylates.

The rates of the E2 reaction for the unsubstituted, *p*-methoxy-, *p*-chloro-, and *m*-bromo-2-phenylethyl iodides, bromides and tosylates in *t*-butyl alcohol are recorded in Tables 3, 4 and 5, respectively. That the rates were clearly second order was shown by the constant value obtained when the rate constant (k) was calculated by applying the second order rate equation to the data. Each rate is the average of two or more runs, and average deviations have been calculated. The rates were measured at two temperatures, where possible, in order that entropies and energies of activation could be calculated.

Since a second order displacement reaction producing an ethyl-2-phenylethyl ether and an elimination reaction giving a styrene can both take place in these solvent-base systems (Eqn. 9), the observed rate of reaction is actually the sum



(Eqn. 9)

of the two rates. From the olefin yields, the rate of elimination can be calculated. Olefin yields were determined spectrophotometrically, and for the iodides and bromides, all of these were 100% within experimental error. The tosylates,

Table 3. Rates of the elimination reaction of $YC_2H_4CH_2CH_2I$ in *t*-butyl alcohol

Y	Base	T. (°C.)	$k_{E2} \times 10^4$ (l./mole-sec.)
H	*t*-BuOK	30	405 ± 10
p-Cl	*t*-BuOK	30	1190 ± 30
p-OCH_3	*t*-BuOK	30	127 ± 2
m-Br	*t*-BuOK	30	2110 ± 70
H	EtOK	30	130 ± 3
p-Cl	EtOK	30	466 ± 10
p-OCH_3	EtOK	30	43.1 ± 0.8
m-Br	EtOK	30	938 ± 39
H	EtOK	50	536 ± 23
p-OCH_3	EtOK	50	206 ± 7

Table 4. Rates of the elimination reaction of $YC_4H_6CH_2CH_2Br$ in *t*-butyl alcohol

Y	Base	T. (°C.)	$k_{E2} \times 10^4$ (l./mole-sec.)
H	*t*-BuOK	30	91.1 ± 2.1
p-Cl	*t*-BuOK	30	274 ± 11
p-OCH_3	*t*-BuOK	30	24.9 ± 0.7
m-Br	*t*-BuOK	30	575 ± 18
H	*t*-BuOK	50	369 ± 8
p-OCH_3	*t*-BuOK	50	112 ± 4
H	EtOK	30	26.2 ± 0.6
p-Cl	EtOK	30	98.6 ± 2.0
p-OCH_3	EtOK	30	7.93 ± 0.17
m-Br	EtOK	30	244 ± 6
H	EtOK	50	115 ± 6
p-OCH_3	EtOK	50	396 ± 14

Table 5. Rates of the elimination reaction of $YC_6H_4CH_2CH_2OTs$ in *t*-butyl alcohol

Y	Base	T. (°C.)	Olefin yield (%)	kE2 x 10^4 (l./mole-sec.)
H	*t*-BuOK	30	100	20.3 ± 0.5
p-Cl	*t*-BuOK	30	100	121 ± 3
p-OCH_3	*t*-BuOK	30	96	3.75 ± 0.19
m-Br	*t*-BuOK	30	100	686 ± 11
H	*t*-BuOK	50	100	110 ± 4
p-OCH_3	*t*-BuOK	50	95	22.1 ± 0.7
H	EtOK	30	75	4.58 ± 0.26
p-Cl	EtOK	30	87	18.7 ± 6
p-OCH_3	EtOK	30	40	0.96 ± 0.01
H	EtOK	50	75	22.2 ± 0.7
p-OCH_3	EtOK	50	42	5.95 ± 0.15

Table 6. Hammett correlations of rates of elimination of 2-phenylethyl compounds at 30.0°C.

Compound	Solvent	Base	ρ	r	-log k_o[a]
OTos	EtOH	EtO^-	2.27 ± 0.08[50]	0.999	4.343
OTos	*t*-BuOH	*t*-BuO^-	3.39 ± .29	.995	2.596
OTos	*t*-BuOH	EtO^-	2.60 ± .06	.999	3.398
Br	EtOH	EtO^-	2.14 ± .15[50]	.989	3.260
Br	*t*-BuOH	*t*-BuO^-	2.08 ± .02	.999	2.043
Br	*t*-BuOH	EtO^-	2.28 ± .12	.997	2.525
I	EtOH	EtO^-	2.07 ± .09[50]	.996	2.497
I	*t*-BuOH	*t*-BuO^-	1.88 ± .06	.999	1.388
I	*t*-BuOH	EtO^-	2.07 ± .09	.999	1.834
$^+S(CH_3)_2$	EtOH	EtO^-	2.75 ± .21[50]	.989	2.330

[a] Calculated value of the intercept.

on the other hand, underwent a sizable amount of displacement as well as elimination, and Table 5 includes olefin precentages. The rates of elimination, k_{E2}, were calculated from the product of the observed rate and the olefin fraction. For the bromides and iodides, the observed rate was equal to the rate of elimination, since the olefin yield was 100%. For the tosylates, however, these two rates were generally different.

The 2-phenylethyldimethylsulfonium salt, which had been studied in ethanol previously,[50] could not be investigated in _t_-butyl alcohol because of a lack of solubility in this solvent.

The data from Tables 3, 4 and 5 were fitted to the Hammett equation.[55] This equation has been used to correlate the rates of a wide variety of reactions of compounds containing substituted benzene rings. It says that the rate

$$\log \frac{k}{k_o} = \rho\sigma$$

constant for the reaction of a benzene compound containing a _meta_ or _para_ substituent (k) is related to that for an unsubstituted benzene compound (k_o) by two constants, ρ and σ. The σ value,[56] which is different for each substituent,

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[55] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, N.Y., p. 184 (1940).

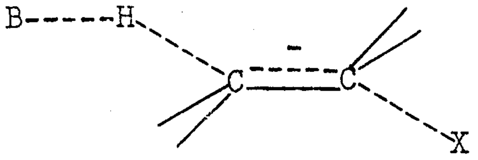
[56] H. H. Jaffe, _Chem. Rev._, _53_, 191 (1953).

is interpreted as being a measure of the ability of the substituent to change the electron density at the reaction center. When log k is plotted versus σ, the slope of the resulting straight line is the ρ-value for the reaction. The ρ-value is a measure of the sensitivity of the reaction to substituents and thus, a measure of the difference in electron density at the phenyl-bearing carbon atom between the ground state and the transition state. A large positive value of ρ indicates a large amount of negative charge is generated at the benzyl carbon atom in the transition state. The ρ-values for the rate data of Tables 3, 4 and 5 were calculated by the method of least squares from a log k versus σ plot. The results of these calculations are reported in Table 6 along with literature values of ρ for these same reactions in ethanol. Correlation coefficients,[56] which are a measure of the fit of the data to a straight line, with a perfit fit having a value of 1.00, are also recorded.

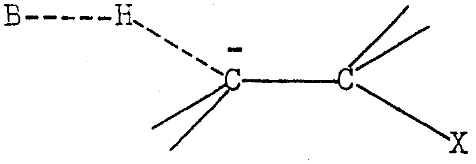
As in the elimination reaction with ethoxide ion in ethanol, the 2-phenylethyl compounds show large positive values of ρ for the reaction with t-butoxide ion in t-butyl alcohol and with ethoxide ion in t-butyl alcohol, showing that β-proton acidity is of importance in determining the rates of elimination.

The results of this study, especially when taken together with the deuterium isotope effect studies of

Saunders and Edison,[57] provide striking confirmation of the dual nature of the transition state of the E2 reaction. In the 2-phenylethyl system, the transition state apparently has a structure somewhere between VII and VIII, with varying



VII



VIII

degrees of double bond character between the two carbons and carbanionic character at the β-carbon atom. Thus, a spectrum of transition states is available to the reaction ranging from the E2 transition state (VII) to the E1cB transition state (VIII).

When the bromides and iodides are reacted with ethoxide ion in ethanol[50] the Hammett ρ-values are nearly identical, showing that the amount of negative charge generated on the β-carbon in the transition state is nearly the same for these two halides. With the stronger base, potassium t-butoxide, in t-butyl alcohol, the reaction rate is increased but the amount of charge on the β-carbon, as measured by ρ, remains the same. Thus, the stronger base would be expected to increase

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[57] W. H. Saunders, Jr. and D. H. Edison, J. Am. Chem. Soc., 82, 138 (1960).

carbon-hydrogen bond breaking at the β-carbon in the transition state, but carbon-halogen bond breaking must also increase in order to keep the charge on the β-carbon atom the same in both systems. This indicates a large amount of double bond character in the halide transition state, since carbon-halogen bond breaking seems to be highly dependent on carbon-hydrogen bond breaking. Even in these highly concerted eliminations, the large positive value of ρ speaks for a great deal of carbanionic character of the β-carbon in the transition state.

These results are to be compared with those for the elimination of the tosylates. In ethanol, the negative charge developed on the β-carbon in the transition state is only slightly greater for the halides. But when the stronger base, potassium t-butoxide is used, the ρ-value increases drastically to 3.39. As carbon-hydrogen bond breaking is increased with the stronger base, much of the extra negative charge generated in the transition state cannot be relieved by the tosylate group and resides on the benzyl carbon atom, thus causing an increase in ρ. In contrast, this extra negative charge must reside on the leaving group in the halide transition state in order to keep the ρ-value the same. It would appear that the transition state for tosylate elimination has more carbanionic character than that for the halides, being closer to VIII. Exactly why the tosylate group cannot absorb this added charge in the transition state, and, therefore, has a less synchronous transition state than the halides, is not entirely clear (vide infra).

Of course, when the stronger base, t-butoxide ion, is used in the reaction, the solvent is changed to t-butyl alcohol. It might be argued that differences in solvating power between ethanol and t-butyl alcohol might be part of the reason for the observed change in ρ. That it is only a small part is shown by the fact that ρ drops nearly to its value in ethanol when the reactions are run in t-butyl alcohol using potassium ethoxide as the base. It is therefore demonstrated that the strength of the base is the major factor involved in the increased ρ-value observed for tosylate elimination.

This evidence, although persuasive in its own right, is quite convincing in light of the recent kinetic isotope effect studies in the 2-phenylethyl system.[57] With ethoxide as a base, the deuterium isotope effect, which is a measure of the amount of carbon-hydrogen bond breaking occurring in the transition state, was smaller for tosylates ($k_H/k_D = 5.66$ at 30°C.) than the bromides ($k_H/k_D = 7.11$) when both β-protons were substituted with deuterium. With the stronger base, potassium t-butoxide, both these values rose, to 8.01 and 7.89, respectively. With both halides and tosylates then, carbon-hydrogen bond breaking increased in the stronger base, but the ρ-values reported herein have shown that only with tosylate does the charge on the β-carbon increase. Perhaps consideration of these results in each solvent-base system separately yields a better understanding of what is happening. With ethoxide in ethanol, the tosylates have a slightly larger amount of negative charge on the benzyl carbon in the transition state; but, at the same time, carbon-hydrogen bond breaking is less complete than for the bromides as shown by the smaller kinetic isotope effect. In the reaction with t-butoxide ion, this same measure of the carbon-hydrogen bond breaking gives the same result for bromides and tosylates. Yet, the ρ -value for the reaction in t-butoxide shows that the tosylate has much more negative charge generated on the β-carbon atom. Thus, an apparent anomoly exists. The tosylate has less carbon-hydrogen bond breaking (as measured by the deuterium isotope effect) and yet, more negative charge at the β-carbon (as measured by ρ) than the bromide in the transition state. A reasonable explanation for these results is that the tosylate group is removing less of the negative charge from the system and, consequently, carbon-leaving group bond breaking has not progressed as far in the transition state as in the case of the bromide.

The ethoxide-t-butyl alcohol system was prepared by adding five volume per cent of ethanol to a solution of approximately .1M t-butoxide in t-butyl alcohol. Since no data are available on the relative acidity of ethanol in *t*-butyl alcohol, it might be argued that *t*-butoxide rather than ethoxide is still the major basic species in this system. Two facts speak against such an argument. In the first place, Table 7 shows that the rates of reaction in ethoxide-*t*-butyl alcohol are five times slower than in *t*-butoxide-*t*-butyl alcohol. If *t*-butoxide ion was still the dominant reactive species, the addition of a small amount of ethanol to the reaction mixture would not be expected to decrease the rate by a factor of five. More importantly, the amount of elimination taking place with ethoxide ion in *t*-butyl alcohol (40-87%) is more like that observed using ethoxide ion in ethanol (20-47%) than with potassium *t*-butoxide in *t*-butyl alcohol (100%).

The entropies and energies of activation for the eliminations in all three solvent-base systems are recorded in Table 8. The values for the tosylates and bromides in ethoxide and ethanol were taken from the literature,[58] while the values for the other solvent-base systems were calculated from the data in Tables 3, 4 and 5. The midpoint of the temperature range of the data, T_m, is included in the table for each case. The enthalpy of activation, $H^{\ddagger}$, was determined from the slope of a log k versus 1/T plot and the

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[58] D. H. Froemsdorf, "Directive Effects in Elimination Reactions", Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa (1959).

Table 7. Relative reactivity of bromides, iodides and tosylates in some displacement and elimination reactions $C_6H_5CH_2CH_2X + B^-$

X	B^-	Solvent	Rel. rate E2	Rel. rate Sn2
OTos	EtO^-	EtOH	1	2
Br	EtO^-	EtOH	11	0.2
I	EtO^-	EtOH	68	0.5
OTos	*t*-BuO^-	*t*-BuOH	52 (1)	
Br	*t*-BuO^-	*t*-BuOH	233 (4.5)	
I	*t*-BuO^-	*t*-BuOH	1030 (20)	
OTos	EtO^-	*t*-BuOH	11 (1)	
Br	EtO^-	*t*-BuOH	61 (5.6)	
I	EtO^-	*t*-BuOH	300 (27)	

equation, $H^{\ddagger} = E_a - RT$. Values for the entropy of activation, $S^{\ddagger}$, were obtained from the intercept of a log k versus 1/T plot.

Table 7 shows that the rates of reaction in the less polar solvent, *t*-butyl alcohol, increase fifteen to fifty-fold. However, this relatively small change in rate is the consequence of large and opposing effects of energy and entropy of activation. For example, comparing the rate of elimination of the bromide in *t*-butoxide in *t*-butyl alcohol with the same reaction in ethoxide in ethanol, it is found that the enthalpy of activation ($H^{\ddagger}$) favors an increase in rate of 10^4. The entropy of activation ($S^{\ddagger}$), on the other

$$F^{\ddagger} = H^{\ddagger} - TS^{\ddagger}$$

Table 8. Enthalpies and entropies of activation for eliminations from $YC_6H_4CH_2CH_2X$

X	Y	Solvent	Base	T (°C.)	$H^{\ddagger}$ kcal./mole	$S^{\ddagger}$ cal./mole °C.
OTs	H	EtOH	EtO^-	42	20.4	-11.2
OTs	H	*t*-BuOH	*t*-BuO^-	40	14.7	-25.2
OTs	H	*t*-BuOH	EtO^-	40	15.8	-18.7
OTs	*p*-OCH_3	EtOH	EtO^-	42	20.4	-13.2
OTs	*p*-OCH_3	*t*-BuOH	*t*-BuO^-	40	16.6	-19.3
OTs	*p*-OCH_3	*t*-BuOH	EtO^-	40	17.1	-25.3
Br	H	EtOH	EtO^-	45	20.4	- 6.8
Br	H	*t*-BuOH	*t*-BuO^-	40	13.0	-25.0
Br	H	*t*-BuOH	EtO^-	40	13.8	-25.0
Br	*p*-OCH_3	EtOH	EtO^-	50	20.8	- 7.3
Br	*p*-OCH_3	*t*-BuOH	*t*-BuO^-	40	14.0	-24.3
Br	*p*-OCH_3	*t*-BuOH	EtO^-	40	15.0	-24.2
I	H	*t*-BuOH	EtO^-	40	13.2	-23.8

hand, is unfavorable by a factor of 10^3, resulting in only a minor change in the rate of reaction. The observed lower entropy of activation is postulated to mean a more ordered transition state, consistent with the theory.

It is important to draw a distinction between the factors that effect the structure of the transition state and the factors that effect the rate of reaction. The results herein indicate that the structure of the transition state is determined by the nature of the leaving group and by the base used, with perhaps the former being more important.

The leaving group apparently effects the transition state in two ways; first, by acidifying the β-protons by an inductive effect and consequently making its removal easier, and secondly, by synchronous bond breaking so that the negative charge is removed from the molecule and resides, to a greater or lesser degree, on the leaving group. The function of the base in determining the structure of the transition state is also very important. With bromides and iodides, the stronger base leads to a transition state with more carbon-hydrogen bond breaking resulting in more double bond character, since these leaving groups can relieve the resulting extra negative charge on the β-carbon atom. On the other hand, with tosylates, carbon-oxygen bond breaking apparently does not increase as fast as carbon-hydrogen bond breaking when the stronger base, _t_-butoxide ion, is used here leading to a transition state with more carbanionic character at the β-carbon atom. These two, leaving group and base, then, determine the structure of the transition state.

In contrast to this, the reaction rate is highly dependent on the nature of the solvent. For example, when the 2-phenylethyl tosylates are reacted with ethoxide ion in ethanol or _t_-butyl alcohol, ρ , which is a measure of the carbanionic character of the transition state is respectively 2.27 and 2.60. When _t_-butoxide is used as base, the value is 3.39, much higher. This is to be contrasted with the rate of reaction in these systems. With t-butyl alcohol as solvent, the rate with ethoxide is 4.5 times slower than that observed when t-butoxide is the base, even though the ρ-values are radically different (2.60 versus 3.39). When the same base but different solvent is used, viz., ethoxide ion in ethanol and in t-butyl alcohol, the rate is observed to be 11 times faster in the latter solvent, even though the ρ-values are much closer together. Furthermore, this increase in rate in a less polar solvent is also noted for the bromides and iodides.

Saunders has noted this same effect in the elimination reaction of 2-phenylethyldimethylsulfonium ion.[50] This compound reacted 10^3 times faster in ethoxide-ethanol than in aqueous sodium hydroxide. Here, of course, the bases used are different. Nevertheless, this difference in base would not be expected to effect the rate by three powers of ten, which leads to the conclusion that large solvent effects are probably being felt. Cristol has also noted this effect of increased rate of elimination in ethanol over water in another system.[60]

The increase in rate in a less polar solvent is in accord

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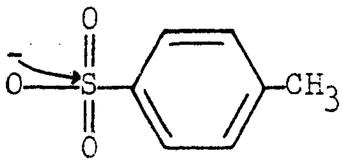
[59] W. H. Saunders, Jr., C. B. Gibbons and R. A. Williams, J. Am. Chem. Soc., 80, 4099 (1958).

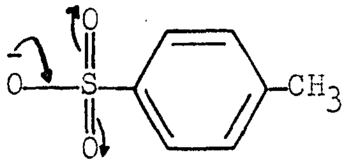
[60] S. J. Cristol and A. Begoon, ibid., 74, 5025 (1952).

with the predictions of Ingold, that the rates of reactions which involve a dispersal of charge in the transition state will be somewhat facilitated by solvents of lesser solvating power.[61]

Returning to the question of why the tosylate group is a better leaving group than bromide under displacement and solvolysis conditions and a poorer one under the conditions of this elimination, let us assume that the stability of the tosylate anion is due to two factors, viz., the strong inductive effect of the adjacent sulfur atom (IX) and the resonance stabilization afforded it by being able to spread the negative charge over three oxygen atoms (X).



IX



X

Suppose we further assume that the resonance stabilization of the anion is strongly dependent on the amount of carbon-oxygen bond breaking in the transition state. Then, when very little carbon-oxygen bond breaking exists in the transition state, only the inductive effect of the sulfur atom is available for stabilizing the anion. Conversely, when

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[61] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell Univ. Press, Ithaca, N.Y., p. 345 (1953).

carbon-oxygen bond breaking is quite extensive, both effects are felt and tosylate is a good leaving group. In solvolytic reactions where the carbon-oxygen is almost completely broken in the transition state, tosylate is a better leaving group than bromide. In elimination reactions, this theory would predict that only the inductive effect of the sulfur atom is available to stabilize the anion and tosylate becomes a poorer leaving group than bromide. Thus, it is suggested that the strong dependence of anion resonance stabilization on the extent of carbon-oxygen bond breaking in the transition state determines the ability of the tosylate as a leaving group.

If the electronic characteristics of the tosylate group are changed somewhat, it might be possible to determine whether or not these ideas are correct. By using a series of leaving groups such as benzenesulfonate, p-toluenesulfonate (tosylate), p-bromobenzenesulfonate, p-nitrobenzenesulfonate and p-methoxybenzenesulfonate, the effect of differences in electron density among the groups might be sufficient to change the electronic characteristics around the sulfur and oxygen atoms; and this, in turn, could markedly change the reactivities of leaving groups through the series. Nevertheless, the present data do suggest that in carefully controlled cases, the bromide-tosylate rate ratio might be used as a measure of the extent of carbon-leaving group bond breaking.

In order to obtain a better correlation of the reactivities of leaving groups in the E2 reaction and to complete the 2-phenylethyl halide series in the ethoxide-ethanol system, the rates of elimination of a series of <u>meta</u> and <u>para</u> substituted 2-phenylethyl chlorides and fluorides were measured under conditions suitable for comparison with the data previously reported for bromides, iodides, tosylates and sulfonium salts. In Table 9 are reported the rates of reaction of these chlorides and fluorides in ethanol using ethoxide ion as base. It was necessary to conduct the reactions at 60°C. and 80°C., because of the slowness of the reactions. As before, each point is the average of two or more runs and all olefin yields were 100 ± 3%, k_{E2} therefore being equal to k_{obs}. Rates at 30°C. were calculated from the data at higher temperatures. For the unsubstituted 2-phenylethyl chloride, a kinetic run at 30°C. yielded a rate constant of 6.67×10^{-6} l./mole-sec., which checks well with the calculated value of 6.8×10^{-6} l./mole-sec. Hammett ρ-values for the reactions at both temperatures were determined by the method of least squares from a plot of log k versus σ. The ρ-values at 30°C. were calculated assuming a linear relationship between T and ρ. These are recorded in Table 10.

Examination of the data reveals that the ρ-value increases monatomically in going from iodide to bromide to chloride to fluoride. This order is also one of increasing

Table 9. Rates of the elimination reaction of $YC_6H_4CH_2CH_2X$ with sodium ethoxide in ethanol solution

Y	X	T. (°C.)	$k_{E2} \times 10^5$ (l./mole-sec.)
H	Cl	60.0	24.1 ± 1.5
p-Cl	Cl	60.0	119 ± 2
m-Br	Cl	60.0	240 ± 9
H	Cl	80.0	185 ± 6
p-Cl	Cl	80.0	855 ± 8
m-Br	Cl	80.0	1810 ± 40
H	Cl	30.0	0.68[a] ±
H	F	60.0	0.45 ± 0.017
p-Cl	F	60.0	2.36 ± .06
m-Br	F	60.0	7.28 ± .15
H	F	80.0	4.22 ± .17
p-Cl	F	80.0	22.6 ± .7
m-Br	F	80.0	67.8 ± 2
H	F	30.0	0.01[a] ±

[a] Calculated from the data at higher temperatures.

electronegativity of the halogens. In the case of fluoride as a leaving group, the observed ρ-value is 3.12, one of the largest ever found for an elimination in ethanol. Thus, the inductive effect of the fluorine and chlorine atoms probably plays a dominant role in the elimination by acidifying the β-hydrogens.

Increased electronegativity of the halogen atoms would also point to increased carbon-halogen bond strength. This is

Table 10. Hammett correlations of the rates of elimination of 2-phenylethyl compounds with ethoxide in ethanol

Compound	T. (°C.)	ρ	r	$-\log k_o$[a]
Cl	60	2.58 ± 0.33	0.991	3.586
Cl	80	2.56 ± .25	.994	2.708
Cl	30	2.61		
F	60	3.10 ± .07	.999	5.360
F	80	3.09 ± .08	.999	4.367
F	30	3.12		
Br	30	2.14 ± .15	.989	3.260
I	30	2.07 ± .09	.999	2.497
$^+S(Me)_2$	30	2.75 ± .21	.989	2.330

[a] Calculated value of the intercept.

Table 11. Entropies and enthalpy of activation for eliminations from $YC_6H_4CH_2CH_2X$

Y	X	T_m (°C.)	$H^‡$ kcal./mole	$S^‡$ cal./mole °C.
H	Cl	70	23.2	-5.6
p-Cl	Cl	70	22.4	-4.8
m-Br	Cl	70	23.0	-1.1
H	F	70	25.3	-5.4
p-Cl	F	70	25.8	-2.5
m-Br	F	70	25.5	-1.2
H	Br	45	20.4[a]	-6.8[a]

[a] From ref. 40.

reflected in the relative rates of elimination, viz., F:Cl:Br:I $\approx$ 1:70:4300:28000. The very slow rate of elimination of fluoride has been noted previously by Chapman and Levy.[62]

The increase in ρ-value throughout the series may also be accounted for in terms of the strength of the carbon-halogen bond. For fluorine as a leaving group, for example, it may be that the increased carbon-halogen bond strength requires a greater "push", i.e., more negative charge built up on the β-carbon in order to react.

The energies and entropies of activation for the chlorides and fluorides are recorded in Table 11 along with T_m in each case. These were calculated as previously described. The data show that the slower rate of elimination of the chlorides and fluorides compared to the bromides and iodides seems to be due entirely to a difference in enthalpy of activation, the entropies being, if anything, slightly more favorable.

That the rates of second order elimination and displacement change in an analogous way in the halogen series is demonstrated by considering the yields of substitution product obtained in each reaction. By gas chromatographic analysis, the small amount of substitution occurring simultaneously with elimination in the reaction of each of the

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[62] N. B. Chapman and J. L. Levy, J. Chem. Soc., 1673 (1952).

2-phenylethyl derivatives was determined. These were found to be 1% substitution for the iodide, 3% for the bromide, 3% for the chloride and 1% for the fluoride. These values are probably good to within 25% of their real values. Among the halogens, then, the amount of substitution occurring compares closely with one another and shows that, despite the acidity of the β-hydrogen being removed, the E2 and Sn2 reactions change in an analogous way as the nature of the leaving group changes. This comparable change in substitution and elimination rates among the halogens was also noted by Hughes and Shapiro in the reaction of some isopropyl halides in basic "60% ethanol" and "80% ethanol".[63]

A comparison of the rates of displacement for the unsubstituted 2-phenylethyl bromide, iodide and tosylate is recorded in Table 7. These calculations show that the tosylate group, in this system at least, is more reactive than either bromide or iodide in the Sn2 reaction. From the olefin yields and the total rates of reaction of the substituted 2-phenylethyl tosylates with ethoxide ion, it is possible to calculate the rates of the Sn2 reaction for the tosylates. These data are shown in a Hammett plot in Figure 1, along with some data from the literature for the reaction of substituted 2-phenylethyl chlorides with sodium iodide in

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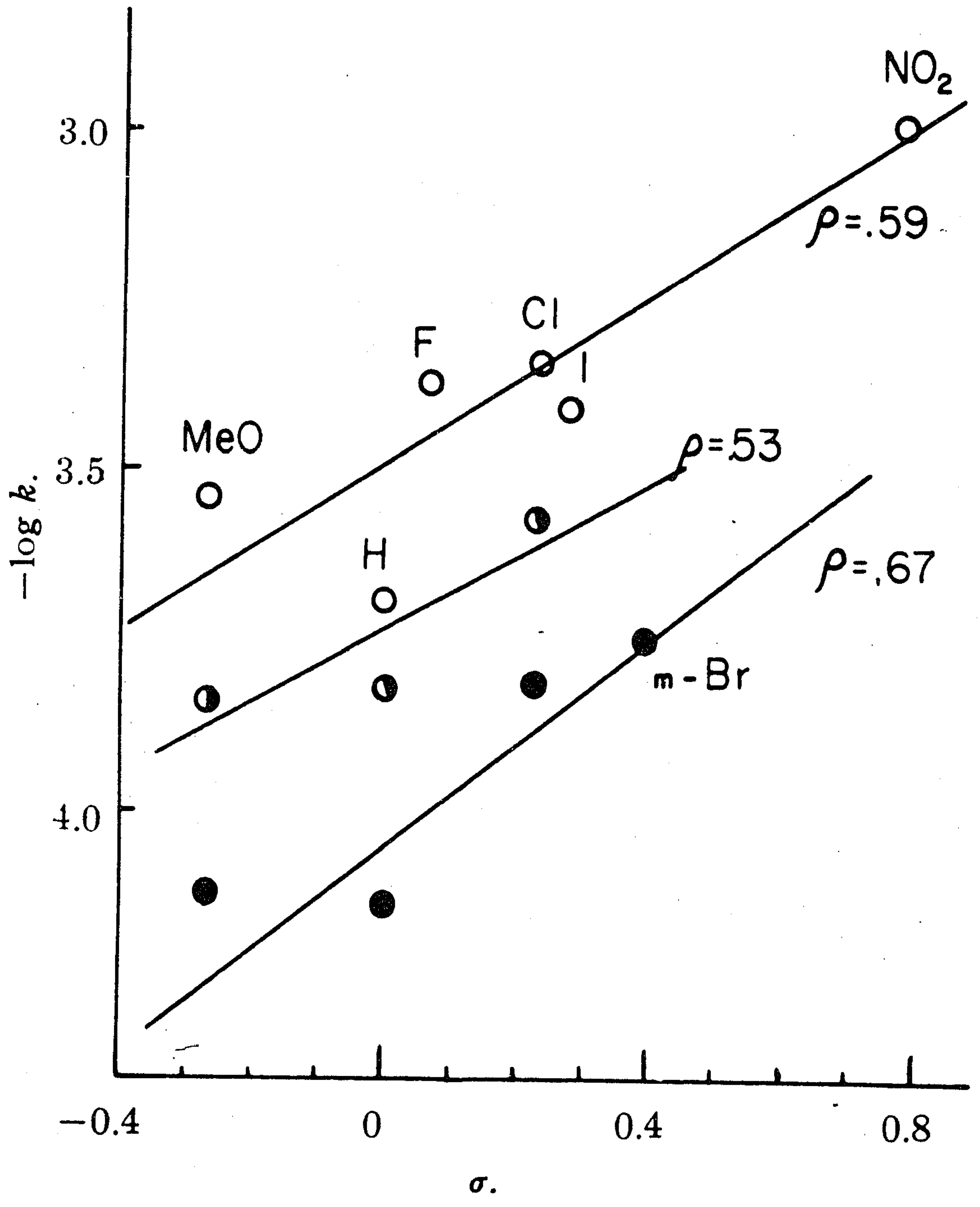
[63] E. D. Hughes and U. G. Shapiro, _ibid._, 1177 (1937).

Figure 1. Hammett plots for the Sn2 displacement of 2-phenylethyl compounds: ○, chlorides with iodide ion in acetone[64]; ◑, tosylates with ethoxide ion in t-butyl alcohol; ●, tosylates with ethoxide ion in ethanol.


NO₂
ρ=.59
F
Cl
I
MeO
ρ=.53
H
ρ=.67
m-Br
3.0
3.5
4.0
−log k.
−0.4
0
0.4
0.8
σ.

acetone.[64] The correlation is admittedly rather poor and leads to slopes of about +0.61. If the p-methoxy points are left out of each series, a somewhat better correlation is obtained with a slope of about +1. The slope is a reasonable one for a transition state which, while insulated from the benzene ring, contains a full negative charge.

The conclusions thusfar have been drawn from reactions of the 2-phenylethyl system in various solvent-base systems. Support for these conclusions can be obtained from a comparison of the relative rates of elimination of various tosylates, bromides, and chlorides in ethanol. Accordingly, a series of rate ratios is compiled in Table 12. These data, most of which were taken from the literature, but including the results from the 2-phenylethyl system, were measured under similar conditions, i.e., in ethanol or aqueous ethanol solution with either hydroxide or ethoxide ion as base, so that it is possible to compare the results.

Table 12 shows that the relative reactivity of bromides and chlorides in elimination reactions remains nearly the same as the β-hydrogens become more acidic. Thus, k_{Br}/k_{Cl} is 41 in the iso-propyl system and 60 in the 2-phenylethyl system. Tosylate reactivity, on the other hand, does not increase as fast as bromide or chloride reactivity with the addition of electron-withdrawing groups to the β-carbon atom.

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[64] G. Baddeley and G. M. Bennett, ibid., 1819 (1935).

Table 12. Relative rates of reaction of some bromides, iodides and tosylates in ethanol

System	Relative E2 rates			Relative overall rates
	k_{Br}/k_{Cl}	k_{Tos}/k_{Cl}	k_{Tos}/k_{Br}	k_{Br}/k_{Cl}
ethyl[a]	--	--	--	29
iso-propyl	41	--	--	39
iso-butyl	--	--	0.94	--
cyclohexyl	--	180	--	--
2-phenylethyl	60	5.7	0.096	60
trans-2-*p*-tolyl sulfonylcyclohexyl	--	1	--	--
cis-2-*p*-tolyl-sulfonylcyclohexyl	--	1	--	--

[a] Ref. 65.

The tosylate to bromide rate ratio is almost 1 in the *iso*-butyl system and drops to 0.1 in the 2-phenylethyl system. The same trend is observed when the tosylates are compared with the chlorides, k_{Tos}/k_{Cl} being 180 for cyclohexyl, 5.7 for 2-phenylethyl and about 1 for the β-sulfones in the last two cases. These observations are in line with the conclusions drawn previously. In systems where a large amount of

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[65] G. H. Grant and C. N. Hinshelwood, *ibid.*, 258 (1933).

negative charge is generated on the β-carbon atom, the tosylate apparently cannot relieve this extra negative charge as well as the halides. Thus, in the last two cases, the chloride overtakes the tosylate in reactivity. But in simpler systems, where greater demands are made on the leaving group, tosylate reactivity increases and is comparable with that of bromide. It is therefore conceivable that there is a whole series of relative tosylate reactivities ranging from more reactive than bromide to less reactive than chloride depending upon the degree of acidity of the β-hydrogens.

In the general study of pyrolytic elimination reactions, few direct comparisons of product distribution and rate with changes in leaving group have been made. Of those that have been done, amides[66, 67] and xanthates[68] were reported to furnish on pyrolysis, olefinic product mixtures nearly identical with those from the corresponding acetate. It seemed surprising that reactions involving temperatures which varied as much as 400°C., and with different atoms involved in the reaction cycle, should give identical product mixtures. To clarify this point and to satisfy the need felt for a

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[66] W. J. Bailey and W. F. Hale, J. Am. Chem. Soc., 81, 651 (1959).

[67] H. E. Baumgarten, F. A. Bower, R. A. Setterquist and R. E. Allen, ibid., 80, 4588 (1958).

[68] C. H. DePuy and R. W. King, Chem. Rev., 60, 431 (1960).

direct comparison of many leaving groups in a model system, a series of derivatives of *sec*-butyl alcohol was examined in order to compare the amounts of 1-butene, *cis*-2-butene and *trans*-2-butene formed. At the same time, the relative rates of pyrolysis of some of these compounds were determined in an attempt to shed some light on the driving forces involved in pyrolytic *cis* eliminations.

When *sec*-butyl acetate was pyrolyzed, a mixture of olefins was formed in nearly quantitative yield containing 57% 1-butene, 28% *trans*-2-butene and 15% *cis*-2-butene. The composition of this mixture is practically independent of reaction conditions and is extremely reproducible. The relative percentages of olefins formed can be explained on the basis of statistical, thermodynamic and steric effects. The transition state for the ester pyrolysis reaction is thought to be highly concerted with little charge separation. Because it has been so widely studied, the pyrolysis mixture of *sec*-butyl acetate was utilized as a standard for this project.

Initially, the effect on product distribution of increasing the strength of the acidic portion was examined. It seemed possible, in view of the fact that esters substituted with electron-withdrawing groups undergo pyrolysis at lower temperatures compared to acetates, that these esters might undergo elimination by more polar mechanisms, leading to a general increase in proportions of 2-butene. Alkyl halides yield predominantly 2-butene and, because of this, are suggested to have a considerable amount of charge separation in the transition state with heterolytic carbon-halogen bond breaking playing an important role.[69] In Table 13 are given the results of the pyrolysis of a series of sec-butyl haloacetates which were especially useful here because of the reasonably graded series of pK_a's obtainable. The monochloroacetate gave very reproducible results, but the pyrolysis of the dichloroacetate and trifluoroacetate were complicated because the olefinic products were found to partially isomerize in the presence of acidic products. Fortunately, the addition of approximately equal amounts of pyridine and/or toluene to the esters before pyrolysis served as a trap or diluent for these acidic products and led to reproducible results. sec-Butyl trichloroacetate could not be studied at all because of the large amounts of hydrochloric acid produced, which led to extensive charring on the pyrolysis column even at temperatures where only minute yields of olefinic products were obtained.

The results in Table 13 show that the relative olefin proportions show remarkably little change from the acetate olefin distribution. Only with the trifluoroacetate is the amount of 2-butene slightly increased. The change in olefin

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[69] A. Maccoll in Theoretical Organic Chemistry: Papers presented to the Kekule Symposium, London, 1958, Butterworth, London, p. 230 (1959).

Table 13. Effect of acid strength on the product distribution in the pyrolysis of *sec*-butyl esters

Ester	T. (°C.)	Additive	1-butene	2-butene trans	2-butene cis
Acetate	450	none	57	28	15
Monochloroacetate	375	none	57	28	15
Dichloroacetate	350	none	52	30	18
	340	pyridine	55	30	15
	425	toluene	54	30	16
	425	pyridine + toluene	56	29	16
Trifluoroacetate	350	none	40-52	31-34	17-26
	335	pyridine + toluene	52	31	17

Table 14. Product distribution in the pyrolysis of some *sec*-butyl esters

Ester	T. (°C.)	Additive	1-butene	2-butene trans	2-butene cis
Benzoate	400	none	52	30	18
Pivalate	460	none	57	28	15

distribution is very small over the series, demonstrating that the direction of elimination in the ester pyrolysis reaction is not sensitive to inductive effects in the acid being eliminated. Apparently, a polar mechanism, such as is suggested for the pyrolysis of alkyl halides, is not available to the ester pyrolysis reaction even when the powerfully acidic trifluoroacetyl group is substituted for the acetyl group.

In Table 14 are reported the results of the pyrolysis of two other esters that might also be expected to lead to somewhat different olefin distributions than the acetate. Again the olefin proportions are practically unchanged. The pivalate pyrolysis demonstrates that a bulky group in the ester has no effect whatsoever on the direction of elimination i.e., no steric effect exists because of substitution at the ester group. No explanation for the slightly greater amounts of 2-butene from the pyrolysis of 2-butyl benzoate can be offered as yet.

Many other derivatives of alcohols have been pyrolyzed to yield olefins. Some of these were examined as derivatives of sec-butyl alcohol, t-amyl alcohol and 2-octyl alcohol. Table 15 is a list of the results of the pyrolysis of these together with literature values for the olefin distributions produced on the pyrolysis of some acetates and amine oxides. Each of the derivatives, viz., vinyl ether (XIII), amide

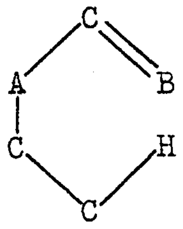
Table 15. Relative percentages of olefins formed in pyrolysis of vinyl ethers, acetamides and xanthates[a]

Compound	Pyrolysis T. (°C.)	1 olefin	2 olefin	
			trans	cis
sec-butyl acetate	450	57	28	15
sec-butyl xanthate	350	41	40	19
sec-butyl vinyl ether	450	47	37	16
sec-butyl acetamide	550	46	34	20
sec-butyl amine oxide (liq. phase)	150	67	21	13
tert-amyl acetate[68]	400	76	24	
tert-amyl xanthate (liq. phase)	135	53	47	
tert-amyl vinyl ether	450	66	34	
2-octyl acetate	490	46	36	18
2-octyl xanthate (liq. phase)	165	34	48	18

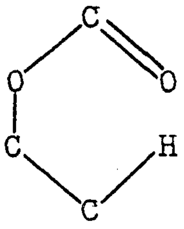
[a] Averages of 2 to 4 runs. In no case did an individual run vary more than 2% from the average.

(XIV) and xanthate (XV), has a different basic reaction cycle (XI) from that of the acetate (XII), although all have analogous structures. The reaction of the most general structure (XI) is shown in Equation 10.

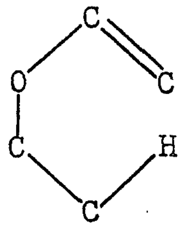
Vinyl ethers on pyrolysis yield olefins and acetaldehyde. Pyrolysis of sec-butyl vinyl ether at 450°C. yielded a mixture



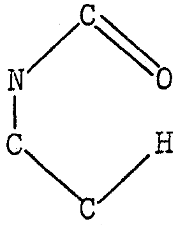
XI



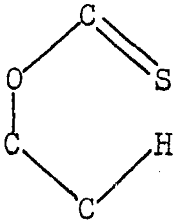
XII



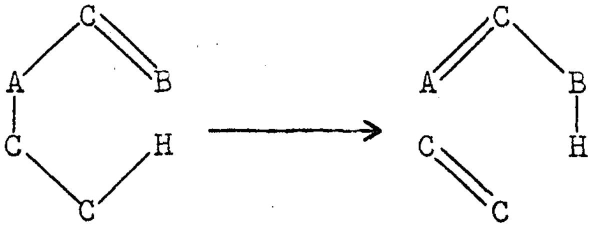
XIII



XIV



XV



(Eqn. 10)

of olefins containing 47% 1-butene, 37% trans-2-butene and 16% cis-2-butene. This result indicates that when an atom in the reaction cycle is changed, a mixture of olefins different from that observed for an acetate might be expected. Indeed, when either nitrogen or sulfur is substituted in the reaction cycle instead of oxygen, giving rise to amides and xanthates, again less 1-olefin was formed than in the pyrolysis of the acetate. The most Saytzeff elimination, i.e., the greatest amount of 2-olefin formed, of any of the derivatives listed in Table 15, was observed in the pyrolysis of the xanthate.

The more Saytzeff elimination in the pyrolysis of the derivatives of sec-butyl alcohol cited in Table 15 was also observed in the pyrolysis of the same derivatives of t-amyl alcohol and 2-octyl alcohol. In the latter case, it was observed that the longer chain length compared to the sec-butyl derivatives produced quite a noticeable decrease in the proportion of 1-olefin, suggesting some sort of steric interference from the extra chain length.

This observation then led to a study of the product distribution in the pyrolysis of a series of 2-acetoxy-n-alkanes. The results of this study are recorded in Table 16. Obviously, as the chain length increases, the approximately statistical olefin distribution obtained in the pyrolysis of sec-butyl acetate is no longer observed. Between sec-butyl acetate and 2-pentyl acetate, a large drop in 1-olefin is observed and this then levels out through 2-octyl acetate, such that acetates above butyl might be considered to produce 48 ± 2% 1-olefin.

The change in olefin proportion observed in this system can be accounted for by consideration of transition state eclipsing effects in a manner analogous to that proposed by Benkeser for the pyrolysis of ethyl-neopentyl carbinyl

Table 16. Relative percentages of olefins formed in the pyrolysis of 2-*n*-alkyl acetates[a]

Compound	% 1-olefin	% *trans*-2-olefin	% *cis*-2-olefin
2-Butyl acetate	57	28	15
2-Pentyl acetate	51	34	15
2-Hexyl acetate	48	37	15
2-Heptyl acetate	49	33	18
2-Octyl acetate	46	36	18

[a] Average of 2 to 4 runs. In no case did an individual run vary more than 2% from the average.

acetate.[70] When applied to the pyrolysis of 2-*n*-alkyl acetates, this argument calls for greater steric assistance from a longer carbon chain in the transition state leading to 2-olefin, but provides no added assistance in the transition state leading to 1-olefin. Thus, a higher proportion of 2-olefin should be observed with increasing chain length, which is the case.

The relative rates of pyrolysis of some *sec*-butyl alcohol derivatives were examined and are collected in Table 17. The increase in rate of only a factor of ten in changing from the

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[70] R. A. Benkeser, J. J. Hazdra and M. L. Burrous, *J. Am. Chem. Soc.*, *81*, 5374 (1959).

Table 17. Relative rates of pyrolysis of some 2-butyl derivatives

Compound	Relative rate
Acetamide	0.04
Acetate	1
Vinyl ether	1.3
Trifluoroacetate	10

acetate to the trifluoroacetate again points up the relative insensitivity of the ester pyrolysis reaction to inductive effects. Amides were found to be less reactive than esters, while vinyl ethers and esters had about the same reactivity. In the latter case, the likeness in rate was not expected in view of the difference in reaction cycles. However, the result again speaks for a transition state with appreciable double bond character.

This work contrasts for the first time a variety of pyrolytic cis eliminations in the same system and provides a reference for future work in this field. The results are in substantial agreement with a picture in which the transition state exhibits appreciable double bond character.

EXPERIMENTAL

Preparation and Purification of Materials

Preparation of 2-arylethyl compounds

2-Arylethanols The 2-arylethanols are available as previously described.[71]

2-Arylethyl p-toluenesulfonates The 2-arylethyl p-toluenesulfonates were prepared from the corresponding alcohol according to Tipson's procedure.[72] The alcohol (10 g.) was added to a solution of 100 ml. of anhydrous pyridine and 1.5 molar equivalents of p-toluenesulfonyl chloride at -5°C. The mixture was swirled in the brine bath for one hour and placed in a freezer overnight. During this time a precipitate of pyridine hydrochloride appeared. The mixture was poured into an ice bath and the p-toluenesulfonate crystallized immediately. The solid was filtered and recrystallized from a pentane-ether mixture.

2-Phenylethyl p-toluenesulfonate, m.p. 38-39°C. (lit.[71] m.p. 38.5-39°C.).

2-(p-Chlorophenyl)-ethyl p-toluenesulfonate, m.p. 79-80 °C. (lit.[71] m.p. 79.3-80.3°C.).

2-(m-Bromophenyl)-ethyl p-toluenesulfonate, m.p. 43-44°C.

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[71] C. H. DePuy and D. H. Froemsdorf, J. Am. Chem. Soc., 79, 3710 (1957).

[72] R. S. Tipson, J. Org. Chem., 9, 235 (1944).

(lit.[71] m.p. 43-44°C.).

2-(p-Methoxyphenyl)-ethyl p-toluenesulfonate, m.p. 58.5-59°C. (lit.[71] m.p. 58.6-59.6°C.).

2-Arylethyl fluorides The 2-arylethyl fluorides were prepared by the action of potassium fluoride on the corresponding p-toluenesulfonate.[73] As a typical example, 5.0 g. (0.04 mole) of 2-phenylethyl p-toluenesulfonate was mixed with 11.2 g. (0.12 mole) of potassium fluoride dihydrate in 25 ml. of diethylene glycol and stirred at 100°C. for 20 hours. At the end of this time, the initially heterogeneous system had become homogeneous. The solution was cooled, poured into 100 ml. of water and extracted with pentane. After washing and drying the extracts, the pentane was carefully removed and the product distilled.

2-Phenylethyl fluoride: 51% yield, b.p. 55-56°C. (12 mm.). Anal. Calcd. for C_8H_9F: C, 77.4; H, 7.30. Found: C, 77.5; H, 7.29.

2-(p-Chlorophenyl)-ethyl fluoride: 43% yield, b.p. 79-80°C. (9 mm.).

Anal. Calcd. for C_8H_8ClF: C, 60.58; H, 5.08; Cl, 22.36. Found: C, 60.88; H, 5.13; Cl, 22.08.

2-(m-Bromophenyl)-ethyl fluoride: 45% yield, b.p. 80-81°C. (4 mm.). An insufficient amount of this compound was

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[73] E. D. Bergmann and I. Shahak, Chem. and Ind., 157 (1958).

available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were calculated from experimental infinity points.

2-Arylethyl chlorides The 2-arylethyl chlorides were prepared by the action of lithium chloride on the corresponding p-toluenesulfonate in a procedure analogous to that for the preparation of the 2-arylethyl fluorides. A 4:1 molar excess of lithium chloride in diethylene glycol was used.

2-Phenylethyl chloride: 69% yield, b.p. 81-83°C. (14 mm.). (lit.[74] b.p. 83-84°C. (14 mm.)).

2-(p-Chlorophenyl)-ethyl chloride: 41% yield, b.p. 82-83°C. (3 mm.) (lit.[74] b.p. 133°C. (35 mm.)).

2-(m-Bromophenyl)-ethyl chloride: 56% yield, b.p. 80-81°C. (1 mm.). An insufficient amount of this compound was available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were determined from experimental infinity points.

2-Arylethyl bromides The 2-arylethyl bromides were prepared by the action of anhydrous lithium bromide on the corresponding p-toluenesulfonate in acetone solution.[75] The

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[74] G. Baddeley and G. M. Bennett, J. Chem. Soc., 1820 (1935).

[75] H. C. Brown and O. H. Wheeler, J. Am. Chem. Soc., 78, 2199 (1956).

products were carefully fractionated.

2-(p-Chlorophenyl)-ethyl bromide, b.p. 79°C. (0.5 mm.) (lit.[71] b.p. 79°C. (0.5 mm.)).

2-(m-Bromophenyl)-ethyl bromide, b.p. 88-89°C. (1 mm.) (lit.[71] b.p. 98-100°C. (1 mm.)).

2-(p-Methoxyphenyl)-ethyl bromide, b.p. 79°C. (1 mm.) (lit.[71] b.p. 79°C. (1 mm.)).

2-Phenylethyl bromide was Eastman Kodak Company White Label which was redistilled, b.p. 65°C. (3 mm.).

2-Arylethyl iodides The 2-arylethyl iodides were prepared by the action of anhydrous sodium iodide on the corresponding tosylate in acetone solution.[75] The products were carefully fractionated.

2-(p-Chlorophenyl)-ethyl iodide, b.p. 84-88°C. (0.5 mm.) (lit.[71] b.p. 115-117°C. (1 mm.)).

2-(m-Bromophenyl)-ethyl iodide, b.p. 105-107°C. (1 mm.) (lit.[71] b.p. 105-110°C. (1 mm.)).

2-(p-Methoxyphenyl)-ethyl iodide, b.p. 87-89°C. (0.5 mm.) (lit.[71] b.p. 117-119°C. (1 mm.)).

2-Phenylethyl iodide, b.p. 95°C. (3 mm.) (lit.[71] b.p. 95°C. (3 mm.)).

Preparation of alkyl p-toluenesulfonates

These compounds were prepared by Tipson's procedure[72] and purified by low temperature recrystallization. As a typical example, 1.5 molar equivalents of p-toluenesulfonyl chloride was dissolved in a solution of 10 g. (.135 mole) of iso-butyl alcohol in 100 ml. of dry pyridine. This solution was swirled in an ice-salt bath at -5°C. for one hour and kept at -10°C. overnight. When the resulting mixture was diluted with ice and water, the p-toluenesulfonate came out of solution as an oil. The product was extracted with chloroform and the extracts washed with cold dilute sulfuric acid, bicarbonate solution and, finally, water. After drying over anhydrous sodium sulfate and removal of the chloroform under reduced pressure, the residue was taken up in pentane. When this solution was cooled to -80°C., the p-toluenesulfonate crystallized and was centrifuged. The pentane was decanted from the solid and the recrystallization procedure repeated four more times. Finally, the last trace of pentane was removed by drying *in vacuo* over paraffin strips.

iso-Butyl *p*-toluenesulfonate, m.p. 11-12°C., b.p. 153-155°C. (2 mm.) (lit.[76] b.p. 163-164°C. (3 mm.)).

iso-Propyl *p*-toluenesulfonate, b.p. decomp., m.p. 16.5-17.5°C. (lit.[77] m.p. 19.9°C.).

n-Propyl *p*-toluenesulfonate, m.p. -7 - -8°C., b.p. 139-141°C. (2 mm.) (lit.[76] b.p. 154-156°C. (3 mm.)).

For the esters listed above, infra red analysis showed no hydroxyl peak.

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[76] H. Gilman and N. J. Baeber, *ibid.*, *47*, 518 (1925).

[77] W. F. Edgell and L. Parts, *ibid.*, *77*, 4899 (1955).

Preparation of esters and related materials

2-Butyl chloroacetate A fractionated sample of 2-butanol (Eastman Kodak White Label) was esterified with chloroacetyl chloride (Eastman Kodak White Label) in pyridine-benzene solution. The ester was fractionated and a center fraction taken of boiling point range 78.5-79°C. (30 mm.) (lit.[78] b.p. 169-160.5°C. (758 mm.)).

2-Butyl dichloroacetate A fractionated sample of 2-butanol was esterified with dichloroacetyl chloride (Eastman Kodak White Label) in pyridine-benzene solution. The ester was fractionated and a center fraction taken of boiling point range 87-87.5°C. (30 mm.). Infra red spectrophotometric analysis showed strong absorptions at 5.67, 5.73 and 8.52 μ, characteristic of an ester of this type. Pyrolysis gave butenes as the only olefinic products.

2-Butyl trichloroacetate A fractionated sample of 2-butanol was esterified with trichloroacetyl chloride (Eastman Kodak White Label) in pyridine-benzene solution. The ester was fractionated and a center fraction taken of boiling point range 85-86°C. (20 mm.) (lit.[78] b.p. 186-188°C. (747 mm.)).

2-Butyl trifluoroacetate A fractionated sample of 2-butanol was esterified with trifluoroacetic anhydride (Matheson, Coleman and Bell). The ester was fractionated,

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[78] S. V. Zavgorodnii, Trudy Voronezh. Gosudarst. Univ. (Acta Univ. Voronegiensis), 10, No. 2, 41 (1938). C.A., 33, 5805 (1939).

and a center fraction taken of boiling point range 92-92.5°C. Infra red spectrophotometric analysis showed strong absorptions at 5.61 μ and 8.60 μ characteristic of an ester substituted with three fluorine atoms in the α-position.

<u>2-Butyl benzoate</u> A fractionated sample of 2-butanol was esterified with benzoyl chloride in pyridine-benzene solution. The ester was fractionated and a center fraction taken of boiling point range 69.5-71°C. (3 mm.) (lit.[79] b.p. 112-116°C. (14 mm.)).

<u>2-Butyl pivalate</u> Pivaloyl chloride was prepared by the action of excess thionyl chloride on pivalic acid. After the reaction was complete, the excess thionyl chloride was removed by distillation and the resulting pivaloyl chloride was added dropwise to a fractionated sample of 2-butanol in pyridine-benzene solution. After the reaction work-up, the ester was fractionated and a center fraction taken of boiling point range 147-149°C. Infra red analysis showed strong absorptions at 5.82 and 8.62 μ, characteristic of an ester group. Pyrolysis gave butenes as the only olefinic products.

<u>2-Pentyl acetate</u> 2-Pentyl alcohol was prepared by the Grignard reaction of <u>n</u>-propyl magnesium bromide and acetaldehyde in ether solution. The alcohol was collected by distillation and a center fraction, b.p. 116.5-117.5°C., was acetylated with acetyl chloride in pyridine-benzene

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[79] A. Spassow, <u>Berichte</u>, 70B, 1926 (1937).

solution. The ester was fractionated and a center fraction taken of boiling point range 131-132.5°C. (lit.[80] b.p. 130-131 (1 atm.)).

2-Hexyl acetate   2-Hexyl alcohol (Eastman Kodak White Label) was carefully fractionated. A center fraction, b.p. 139.5-140°C., was acetylated with acetyl chloride in pyridine-benzene solution. The ester was fractionated and a center fraction taken, b.p. 153.5-155°C. (1 atm.) (lit.[80] b.p. 57°C. (20 mm.)).

2-Heptyl acetate   2-Heptyl alcohol was prepared by the Grignard reaction of n-pentyl magnesium bromide and acetaldehyde in ether solution. The alcohol was collected by distillation and a center fraction of b.p. 156-157°C. was acetylated with acetyl chloride in pyridine-benzene solution. The ester was fractionated and a center fraction taken b.p. 171-173°C. (1 atm.) (lit.[80] b.p. 171-173°C. (1 atm.)).

2-Octyl acetate   2-Octyl alcohol (Eastman Kodak Practical Grade) was carefully fractionated and a center fraction collected, b.p. 178-179°C. The alcohol was acetylated with acetyl chloride in pyridine-benzene solution. Fractional distillation of the ester gave the product, b.p. 79-80°C. (13 mm.) (lit.[80] b.p. 84°C. (15 mm.)).

tert-Butyl acetate   This ester was prepared by the

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[80] R. H. Pickard and J. Kenyon, J. Chem. Soc. 105, 852 (1914).

action of acetyl chloride on tert-butanol in pyridine-benzene solution. The ester was collected by distillation, b.p. 96-97.5°C. (1 atm.) (lit.[81] b.p. 97-97.5°C. (1 atm.)).

Purification of materials

Anhydrous ethanol The last trace of water was removed from "absolute" ethanol by the method of Manske using sodium ethoxide and diethyl phthalate.[82]

Anhydrous tert-butanol tert-Butanol (Eastman Kodak White Label) was fractionally distilled, a sharp center fraction being taken, b.p. 83°C. (1 atm.). This sample was then distilled at least twice from metallic sodium under anhydrous conditions. Rate constants run in tert-butanol which was distilled only once from sodium were as much as 10% slower. However, there was no difference in rate constants between doubly and triply distilled samples.

2-Butanol Commercial 2-butanol was fractionated and a center fraction taken of constant boiling point, 99°C. (750 mm.) (lit.[83] b.p. 100°C.).

2-Butyl acetate 2-Butyl acetate (Eastman Kodak White Label) was distilled before use, b.p. 111-112°C. (1 atm.).

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[81] C. R. Hauser, B. E. Hudson, B. Abramovitch and J. C. Shivers, Organic Syntheses, 24, 19 (1944).

[82] R. H. Manske, J. Am. Chem. Soc., 53, 1106 (1931).

[83] A. J. King, J. Chem. Soc., 115, 1409 (1919).

Preparation of vinyl ethers

sec-Butyl vinyl ether   This compound was prepared by the method of Watanabe and Conlon.[84] A solution of 3 g. of mercuric acetate, 37 g. (0.5 mole) of 2-butanol and 144 g. (2 moles) of ethyl vinyl ether was heated at reflux for six hours. Most of the excess vinyl ether was removed by distillation; the residue was taken up in ether and washed well with water. After drying this solution over magnesium sulfate, distillation gave sec-butyl vinyl ether, b.p. 81-83°C. (lit.[85] b.p. 81-81.5°C.). For the pyrolysis experiments, the vinyl ether was purified by preparative gas phase chromotography on 1 meter of 20% THEED followed by 2 meters of Ucon LB550X.

tert-Amyl vinyl ether   A procedure analogous to the above was used for the preparation of tert-amyl vinyl ether. It was also purified by preparative gas phase chromatography. Physical properties: b.p. 102°C. (micro boiling point determination); $[n]_D^{20} = 1.4106$. An insufficient amount of this material was available for purification of an analytical sample. Pyrolysis, however, afforded only acetaldehyde, 2-methyl-2-butene and 2-methyl-1-butene. Infra red

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[84] W. H. Watanabe and L. E. Conlon, J. Am. Chem. Soc., 79, 2828 (1957).

[85] M. E. Shostakovskii, B. T. Mikhant'ev and N. N. Ovchinnekova, Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 1099 (1952).

spectrophotometric analysis of the pure compound showed strong absorptions at 6.14 μ characteristic of olefinic linkages and at 8.63 μ, characteristic of ether linkages as well as very strong absorptions in the carbon-hydrogen region.

Preparation of xanthates

2-Butyl xanthate 2-Butyl xanthate was prepared by the Whitmore modification of the Chugaev reaction,[86, 87] b.p. 57-59°C. (4 mm.). Pyrolysis afforded a mixture of butenes as the only olefinic products.

tert-Amyl xanthate Potassium, 8.5 g. (0.21 mole), was dispersed in 150 ml. of xylene and 18 g. (0.26 mole) of *tert*-amyl alcohol added dropwise without stirring. The temperature was raised to 65°C. and the reaction was complete in two hours. The mixture was diluted with 150 ml. of *n*-butyl ether and 30.5 g. of carbon disulfide was added dropwise. After standing overnight, 57 g. (0.40 mole) of methyl iodide was added slowly and the mixture stirred for six hours. The reaction mixture was filtered and used directly in the pyrolysis reaction, since the product was not stable to distillation. Pyrolysis afforded 2-methyl-2-butene and 2-methyl-1-butene as the only olefinic products.

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[86] R. A. Benkeser, J. J. Hazdra and M. L. Burrous, *J. Am. Chem. Soc.*, **81**, 5374 (1959).

[87] F. C. Whitmore and C. T. Simpson, *J. Am. Chem. Soc.*, **55**, 3809 (1933).

2-Octyl xanthate   This compound was prepared according to the procedure of Whitmore and Simpson.[87] It was not stable to distillation, decomposing at 165°C. and so, was pyrolyzed from solution.

Preparation of amides

2-Butyl acetamide   2-Butyl acetamide was prepared by the action of acetic anhydride on 2-butyl amine.[88] The product was collected by distillation, b.p. 71.5-72°C. (2 mm.) (lit.[89] b.p. 119°C. (18 mm.)).

Procedures and Equipment

Measurement of reaction rates

Base catalyzed elimination reactions   A solution 0.05 molar in desired compound and 0.1 molar in base was prepared in the following manner. The desired compound (0.005 mole) was weighed accurately into a 100 ml. volumetric flask and dissolved in 50 ml. of solvent. After equilibration at the reaction temperature, this solution was diluted to the calibration mark of the volumetric flask with 0.2M base.

If the rate constant was 10^{-4} liter/mole sec. or slower, 5 ml. samples of the reaction mixture were pipeted into tubules of 8 ml. capacity, sealed off immediately and placed

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[88] W. C. G. Baldwin, Proc. Royal Soc. (London), A162, 215 (1937).

[89] E. H. White, J. Am. Chem. Soc., 77, 6008 (1955).

in the constant temperature bath. If the rate constant was faster than 10^{-4} liter/mole sec., 5 ml. samples were withdrawn directly from the reaction flask at appropriate intervals.

The kinetics were followed by quenching a sample in ice water and titrating the excess base with standard hydrochloric acid. Infinity points were taken experimentally and checked well with calculated values.

In kinetic runs made at 60°C. and 80°C., all solutions were equilibrated and pipeted at 30°C. Appropriate corrections for volume expansion were made in the rate calculations.

All rates were clearly second order as evidenced by the constant values obtained when the integrated form of the second order rate equation was applied to the data. Rates were calculated by taking the average of the individual rates calculated from each point.

$$kt = \frac{2.303}{a-b} \log \frac{b\ (a-x)}{a\ (b-x)}$$

The Hammett equation[55] was applied to the data. Log k was plotted versus σ and the slope, ρ , was obtained by the method of least squares.

$$\log \frac{k}{k_o} = \rho\,\sigma$$

Spectral determination of styrenes A completely reacted sample of 2-phenylethyl compound in base was diluted to approximately 10^{-5} molar with 95% ethanol and analyzed on a Beckman Model DU Spectrophotometer. The extinction coefficients as determined by Saunders and Williams[90] were used: styrene, 13800 at 248 mμ; p-chlorostyrene, 19700 at 253 mμ; p-methoxystyrene, 19200 at 258 mμ. The extinction coefficient of m-bromostyrene was determined from a completely reacted sample of 2-(m-bromophenyl)-ethyl fluoride in sodium ethoxide: C = 14,050 at 248 mμ.

Relative amounts of styrene and ethyl 2-phenylethyl ether formed in the reaction of unsubstituted 2-phenylethyl compounds were determined by gas phase chromatography. The gas chromatograph was calibrated with a mixture from the reaction of 2-phenylethyl p-toluenesulfonate with ethoxide, for which the ether-olefin ratio could be accurately determined spectrophotometrically.

Then a completely reacted solution of 0.2 molar 2-phenylethyl compound and 0.4 molar ethoxide was diluted with water and extracted with pentane. The pentane extracts were dried and carefully concentrated by fractionation of the pentane. The solution, still containing large amounts of pentane, was analyzed on a column of 1/3 silicone oil and 2/3 Apiazon L on firebrick at 185°C.

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[90] W. H. Saunders and R. A. Williams, J. Am. Chem. Soc., 79, 3712 (1957).

Displacement reactions in acetone Several 5 ml. samples of a 0.05 molar solution of potassium iodide in dry purified acetone were pipeted into reaction tubes of 12 ml. capacity. A 0.1 molar solution of the desired compound in acetone (5 ml.) was then added to each tube. These were immediately sealed off and placed in a constant temperature bath at 40°C. After equilibration and mixing for a period of one minute, the first sample was withdrawn and analyzed. Samples thereafter were withdrawn at appropriate intervals.

Analyses were carried out by the adsorption indicator method. A tube was broken and its contents diluted with chlorine free distilled water. This solution was titrated with .03 molar silver nitrate solution to the eosin end point.

All rates were clearly second order as evidenced by the constant values obtained when the integrated form of the second order rate equation was applied to the data. Calculated infinity points were used but agreed well with those taken experimentally.

Equipment and procedures for pyrolyses

Pyrolysis column and vacuum line The pyrolysis column was a vertically mounted, externally heated glass tube 24 inches in length and 3/4 inch in diameter. It was packed for 12 inches of its length with pyrex glass helices. The internal temperature of the column was determined by a thermocouple attached to the heated length of the column. A trap at the bottom of the pyrolysis column led to a vacuum line which was provided with two more traps and an outlet.[91]

Procedure for pyrolysis Pyrolyses were carried out by dropping the liquids at a rate of 1-2 ml. per minute onto the column which was previously heated to the desired temperature. Dry purified nitrogen was passed slowly through the column during the pyrolysis and the products were collected in a Dry Ice trap at the bottom of the column.

When the products were butenes or pentenes, they were distilled under reduced pressure into the vacuum line and collected in gas sampling tubes.

When the products were higher boiling olefins, the pyrolysate was taken up in cold ether and the acetic acid removed by extraction with bicarbonate solution. This ether solution, after being dried over anhydrous sodium-sulfate, was analyzed for olefins by gas phase chromatography. The large amount of ether relative to olefins in this solution did not interfere with the analysis, since the ether had a much shorter retention time than the olefins on the column that was used.

tert-Amyl xanthate and 2-octyl xanthate were pyrolyzed in liquid phase by heating their xylene or toluene solutions

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[91] D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, J. Am. Chem. Soc., 81, 643 (1959).

and collecting the olefins produced.

Determination of olefin distribution by gas phase chromatography Olefinic products were analyzed by gas phase chromatography on a Perkin-Elmer Vapor Fractometer model 154C. A five meter column of dibutyl formamide on Celite was used at room temperature for the butenes and pentenes. For higher boiling olefins, a two meter silver nitrate in diethylene glycol on Celite or dimethyl sulfoxide on Celite column was used. The relative amount of olefins was determined from the areas under the peaks.

As a test of the assumption that the isomeric olefins should have equal thermal conductivity, known mixtures of *trans*-2-octene and 1-octene were prepared from authentic olefin samples obtained from preparative gas phase chromatography. The peak area ratios of these mixtures obtained by gas phase chromatographic analysis showed that the thermal conductivities of these were also equal.

Relative rates of pyrolytic reactions Relative rates of pyrolysis of *sec*-butyl trifluoroacetate versus *tert*-butyl acetate, *sec*-butyl acetamide versus *n*-butyl acetate and *sec*-butyl vinyl ether versus *sec*-butyl acetate were determined by an internal competition method. As a typical example, a 3:1 molar mixture of *sec*-butyl trifluoroacetate and *tert*-butyl acetate was pyrolyzed and its per cent conversion determined both by weighing the butenes and by titrating the acetic acid produced. These two results checked. The olefins produced were analyzed by gas phase chromatography and the amount of 1-butene and 2-butene versus isobutene was measured. From these data, the relative rate was calculated as described by Lee.[92] The relative rate of sec-butyl acetamide versus n-butyl acetate was determined by an analogous procedure.

For the relative rate of sec-butyl vinyl ether versus sec-butyl acetate, the reactants were mixed in equimolar quantities with toluene as an internal standard, and the amount of each reactant in the mixture was measured by gas phase chromatography both before and after pyrolysis. The relative rate was then determined as above.

The relative rates of primary: secondary: tertiary acetates has been determined.[69] From these data, the rates of pyrolysis of these esters relative to sec-butyl acetate were calculated.

Kinetic Data

The rates of the base-promoted elimination reactions of the 2-phenylethyl derivatives in the various solvent base systems reported in this thesis are all the averages of two or more kinetic runs. The rates of reaction and amount of elimination product for a typical run for each unsubstituted compound are summarized in Tables 18 through 32. The volumes

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[92] T. S. Lee in "Technique of Organic Chemistry, Vol. 8," Interscience Publishers, New York, N.Y., p. 100 (1953).

of titrant reported in the second column of each table are the amounts of hydrochloric acid required to neutralize five milliliter aliquots of reaction mixture. Also included are the normality of the titrant, initial concentrations of 2-phenylethyl compound and base, per cent olefin, the second order rate constants calculated for each point and the average rate constant.

Table 18. Rate of reaction of 2-phenylethyl fluoride in sodium ethoxide-ethanol solution at 60°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^6k (liter mole^{-1}sec.$^{-1}$)
0	7.30	--
84360	7.165	4.58
170220	7.045	4.47
251820	6.945	4.37
343620	6.82	4.55
425400	6.75	4.34
592200	6.56	4.57
678240	6.515	4.33
764220	6.46	4.31
(calc.)	5.40	--
Rate over entire period[b]		4.44 ± .12
Rate corr. for vol. expansion (30° to 60°C.)		4.60 ± .12

[a] N_{HCl} = 0.1320; conc. of halide = 0.0501 M; conc. of base = 0.1928M.

[b] Product contained 98% styrene.

Table 19. Rate of reaction of 2-phenylethyl fluoride in sodium ethoxide-ethanol solution at 80°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^5k (liter $\text{mole}^{-1}\text{sec.}^{-1}$)
0	3.22	--
87780	2.75	3.90
158940	2.48	3.89
255300	2.22	3.83
336480	2.055	3.79
504900	1.78	3.93
764100	1.52	4.10
(calc.)	1.07	--
Rate over entire period[b]		3.91 ± .11
Rate corr. for vol. expansion (30° to 80°C.)		4.13 ± .11

[a] N_{HCl} = 0.1214; conc. of halide = 0.0523 M; conc. of base = 0.0782 M.

[b] Product contained 100% styrene.

Table 20. Rate of reaction of 2-phenylethyl chloride in sodium ethoxide-ethanol solution at 60°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^4k (liter $\text{mole}^{-1}\text{sec.}^{-1}$)
0	5.035	--
2520	4.86	2.70
6480	4.635	2.60
10620	4.44	2.55
15540	5.23	2.58
25860	3.91	2.54
71880	3.245	2.40
	2.80	--
Rate over entire period[b]		2.57 ± .10
Rate corr. for vol. expansion (30° to 60°C.)		2.66 ± .10

[a] N_{HCl} = 0.1214; conc. of halide = 0.0543 M; conc. of base = 0.1224 M.

[b] Product contained 94% styrene.

Table 21. Rate of reaction of 2-phenylethyl chloride in sodium ethoxide-ethanol solution at 80°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1}sec.$^{-1}$)
0	5.51	--
900	5.095	1.78
1740	4.785	1.82
2700	4.51	1.84
3300	4.375	1.84
3900	4.285	1.76
5580	4.02	1.77
9060	3.70	1.76
12240	3.54	1.75
	3.28	--
Rate over entire period[b]		1.79 ± .04
Rate corr. for vol. expansion (30° to 80°C.)		1.89 ± .04

[a] N_{HCl} = 0.1214; conc. of halide = 0.0542 M; conc. of base = 0.1335 M.

[b] Product contained 100% styrene.

Table 22. Rate of reaction of 2-phenylethyl bromide in potassium *t*-butoxide-*t*-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1}sec.$^{-1}$)
0	3.54	--
300	3.19	8.79
600	2.92	9.00
900	2.72	8.99
1320	2.495	9.22
1980	2.28	9.03
2940	2.08	9.00
4980	1.87	9.19
	1.73	--
Rate over entire period[b]		9.03 ± .10

[a] N_{HCl} = 0.1214; conc. of halide = 0.0439 M; conc. of base = 0.0859 M.

[b] Product contained 100% styrene.

Table 23. Rate of reaction of 2-phenylethyl bromide in potassium t-butoxide-t-butyl alcohol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	2.505	--
177	1.90	3.77
445	1.44	3.76
603	1.26	3.91
788	1.13	3.87
1022	1.02	3.79
1367	.91	3.71
1567	.86	3.72
1981	.80	3.55
2642	.725	3.65
	.60	--
Rate over entire period[b]		3.76 ± .11

[a] N_{HCl} = 0.1320; conc. of halide = 0.0503 M; conc. of base = 0.0672 M.

[b] Product contained 100% styrene.

Table 24. Rate of reaction of 2-phenylethyl bromide in potassium ethoxide-t-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1}sec.$^{-1}$)
0	3.15	--
840	2.85	2.81
1740	2.62	2.57
2700	2.425	2.67
3780	2.255	2.64
5100	2.085	2.65
6480	1.94	2.69
10980	1.665	2.65
14880	1.53	2.64
19020	1.43	2.72
	1.25	--
Rate over entire period[b]		2.67 ± .07

[a] N_{HCl} = 0.1214; conc. of halide = 0.0462 M; conc. of base = 0.0765 M.

[b] Product contained 100% styrene.

Table 25. Rate of reaction of 2-phenylethyl bromide in potassium ethoxide-t-butyl alcohol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	4.54	--
120	4.31	0.98
240	4.11	1.01
360	3.95	1.00
600	3.64	1.10
840	3.43	1.13
1140	3.25	1.14
1440	3.13	1.13
1800	3.02	1.14
2460	2.91	1.10
	2.75	--
Rate over entire period[b]		1.08 ± .06

[a] $N_{HCl} = 0.1320$; conc. of halide = 0.0472 M; conc. of base = 0.1199 M.

[b] Product contained 100% styrene.

Table 26. Rate of reaction of 2-phenylethyl iodide in potassium-t-butoxide-t-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	2.78	--
240	2.07	3.82
458	1.73	3.94
780	1.45	4.09
1050	1.32	4.16
1293	1.25	4.12
1530	1.205	4.04
1980	1.14	4.05
2400	1.115	3.87
	1.05	--
Rate over entire period[b]		4.01 ± .12

[a] $N_{HCl} = 0.1214$; conc. of halide = 0.0421 M; conc. of base = 0.0676 M.

[b] Product contained 100% styrene.

Table 27. Rate of reaction of 2-phenylethyl iodide in potassium ethoxide-t-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	3.96	--
90	3.74	1.25
210	3.46	1.37
330	3.26	1.34
480	3.04	1.35
720	2.79	1.33
1080	2.52	1.32
1440	2.35	1.29
1920	2.175	1.30
2520	2.04	1.30
3720	1.895	1.29
	1.76	--
Rate over entire period[b]		1.32 ± .04

[a] N_{HCl} = 0.1214; conc. of halide = 0.0534 M; conc. of base = 0.0962 M.

[b] Product contained 100% styrene.

Table 28. Rate of reaction of 2-phenylethyl iodide in potassium ethoxide-t-butyl alcohol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	2.29	--
150	1.775	4.89
270	1.52	5.01
390	1.345	5.08
540	1.17	5.41
780	1.03	5.28
1080	.925	5.14
1410	.84	5.31
1920	.77	5.45
	.69	--
Rate over entire period[b]		5.20 ± .20

[a] N_{HCl} = 0.1320; conc. of halide = 0.0422 M; conc. of base = 0.0604 M.

[b] Product contained 100% styrene.

Table 29. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1}sec.$^{-1}$)
0	4.23	--
600	4.01	1.92
1200	3.80	2.05
2100	3.57	2.01
3300	3.305	2.07
4800	3.085	2.02
6600	2.87	2.06
7800	2.78	2.02
17700	2.37	2.06
	2.21	--
Rate over entire period[b]		2.03 ± .05

[a] N_{HCl} = 0.1214; conc. of tosylate = 0.0491 M; conc. of base = 0.1029 M.

[b] Product contained 100% styrene.

Table 30. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium t-butoxide-t-butyl alcohol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^2k (liter mole^{-1}sec.$^{-1}$)
0	4.21	--
240	3.83	1.10
480	3.57	1.08
720	3.375	1.08
960	3.24	1.06
1200	3.12	1.07
1500	2.99	1.13
1800	2.90	1.16
2160	2.835	1.15
	2.65	--
Rate over entire period[b]		1.10 ± .04

[a] N_{HCl} = 0.1320; conc. of tosylate = 0.0412 M; conc. of base = 0.1110 M.

[b] Product contained 100% styrene.

Table 31. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium ethoxide-t-butyl alcohol solution at 30°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^4k (liter mole^{-1}sec.$^{-1}$)
0	3.42	--
2100	3.23	6.54
4200	3.065	6.10
7920	2.86	6.31
12300	2.635	6.13
15420	2.53	6.04
22380	2.33	6.35
96180	1.675	--
	1.59	--
Rate over entire period[b]		6.27 ± .29

[a]NHCl = 0.1214; conc. of tosylate = .0445 M; conc. of base = .0831 M.

[b]Product contained 75% styrene.

Table 32. Rate of reaction of 2-phenylethyl p-toluenesulfonate in potassium ethoxide-t-butyl alcohol solution at 50°C.

Time elapsed (sec.)	Volume of titrant[a] (ml.)	10^3k (liter mole^{-1}sec.$^{-1}$)
0	3.84	--
240	3.70	3.03
600	3.515	3.05
1080	3.32	2.96
1980	3.005	3.07
2820	2.81	3.00
3900	2.65	2.81
4980	2.52	2.72
6300	2.36	2.81
	1.84	--
Rate over entire period[b]		2.93 ± .13

[a]NHCl = 0.1320; conc. of tosylate = 0.0528; conc. of base = 0.1013 M.

[b]Product contained 75% styrene.

SUMMARY

The base-catalyzed elimination reaction of a series of *meta* and *para* substituted 2-phenylethyl iodides, bromides and tosylates with *t*-butoxide ion in *t*-butyl alcohol and with ethoxide ion in *t*-butyl alcohol was investigated and compared with earlier work on these compounds using ethoxide ion in ethanol. The Hammett ρ-value was calculated in each case and, for the tosylates, was found to increase from 2.3 in ethoxide-ethanol to 3.4 in *t*-butoxide-*t*-butanol while the halide ρ-values remained the same ($\sim$ 2.1). That the change in ρ-value observed for the tosylates was primarily due to the strength of the base was shown by conducting the experiments in *t*-butyl alcohol using ethoxide ion as base. Here, the bromide and iodide ρ-values again remained the same while the tosylate ρ-value dropped to 2.6, almost its value in ethanoxide-ethanol. The results indicate that the halides probably have more double bond character in the transition state, the halide leaving group being better able to relieve negative charge generated on the β-carbon atom in the transition state.

The diminished reactivity of the tosylate group in elimination reactions (compared with solvolytic reactions) was demonstrated not only in the 2-phenylethyl system, but also in simple aliphatic systems. This behavior was explained by postulating a variation in resonance and inductive stabilization of the anion with differences in carbon-oxygen bond breaking.

The rates of reaction of substituted 2-phenylethyl chlorides and fluorides were also measured using ethoxide ion in ethanol. Among the halides, an increase in the rate of reaction and a decrease in ρ-value in going from fluoride to iodide was explained in terms of carbon-hydrogen bond breaking and carbon-halogen bond strength.

The relative reactivities of the 2-phenylethyl chlorides, bromides and tosylates were compared with their reactivities in other alkyl systems. It was shown that the tosylate becomes progressively less reactive compared to the bromide and chloride as the β-hydrogens become more acidic, again demonstrating that the tosylate group cannot relieve negative charge generated on the β-carbon atom in the transition state as well as the halides.

The olefin distributions and relative rates of reaction in the pyrolysis of some substituted esters and other derivatives of *sec*-butyl alcohol were determined. This work contrasted for the first time a variety of pyrolytic *cis* eliminations in the same system. The results showed the absence of large inductive effects due to changes in substituents in the ester group and thus emphasized the concerted nature of the reaction. Compared to the acetate, little change in olefin distribution was observed for the vinyl ether, acetamide and xanthate showing that these derivatives likely undergo pyrolytic elimination by a mechanism similar to esters.

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