ELECTRONIC EFFECTS IN E2 REACTIONS

II. t-BUTOXIDE-INDUCED ELIMINATIONS OF 2-METHYL-3-PENTYL ARENESULFONATES^{1,2}

Allan K. Colter and Donald R. McKelvey

Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania Received November 13, 1964

Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

As part of a study of the influence of electronic effects imposed by the leaving group on As part of a study of the influence of electronic effects imposed by the leaving group on orientation in E2 reactions, a study of elimination in a series of 2-methyl-3-pentyl arenesulfonates (I) has been carried out. The compositions of the olefin mixtures resulting from reaction of selected members of this series with potassium *t*-butoxide in *t*-butanol (Ia, Id), 50% (by volume) *t*-butanol – dioxane (Ia–Ig), 25% (by volume) *t*-butanol – dioxane (Id–Ig), and 25% (by volume) *t*-butanol – dimethyl sulfoxide (Ia, Id, If, Ig), at 50 °C, have been determined using vapor phase chromatography. Second-order rate constants were measured for these reactions in *t*-butanol (Ie, and 50% *t*-butanol – dioxane (Ia, Ia, Ie) at 25 °C. The compositions of the olefin mixtures vary in a fairly regular way with changes in the electronic nature of the leaving group, the fraction of 2-methyl-2-pentene and ratio of *trans*-to *cis*-4-methyl-2-pentene for the most part increasing with increasing electron withdrawal. The E2 reactions in 25% *t*-butanol – dimethyl sulfoxide produce *trans*-and *cis*-4-methyl-2-pentene in ratios (20 to 35) considerably higher than those in an equilibrium mixture (ca. 6).

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The results are discussed in terms of recent views on the E2 transition state.

INTRODUCTION

In recent years, the concept of a continuous spectrum of transition states for the E2 reaction (Fig. 1), differing in the extent to which the C_{β} —H and C_{α} —X bonds are broken, has become widely accepted (1-13). Factors expected to influence the position of an



FIG. 1. Spectrum of E2 transition states.

elimination among the spectrum of transition states and methods of assessing the quality of the transition state have recently been discussed by Bunnett (12). In E2 reactions in alkyl systems having two or more constitutionally nonequivalent β -hydrogens, it is generally agreed that transition states in the E1cb-like region favor abstraction of the most acidic hydrogen, thereby leading to predominant amounts of the product having the smallest number of alkyl groups attached to the olefinic function (Hofmann pattern). Transition states in the synchronous to E1-like regions favor formation of the most highly alkylated olefin (Saytzeff pattern).

In this and previous work (13) we have been concerned with evaluating the importance of electronic effects imposed by the leaving group in determining orientation in E2

¹Part I in this series: A. K. Colter and R. D. Johnson, J. Am. Chem. Soc. 84, 3289 (1962). ²Abstracted from a thesis submitted by Donald R. McKelvey in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1964.

Canadian Journal of Chemistry. Volume 43 (1965)

1283

reactions. Our approach has been to examine the olefin mixtures produced from E2 reactions of a series of alkyl arenesulfonates differing only in a substituent in the meta or para position of the benzene ring in the leaving group. In this way, steric influences (14) are constant throughout the series.

Applied to a series of alkyl arenesulfonates, the model of the E2 transition state discussed by Bunnett does not lead to a clear-cut prediction about how direction of elimination should change with leaving group. Whereas a change to a leaving group of greater electron-attracting character, by increasing the acidity of the β -hydrogens, is predicted to result in a shift toward the E1*cb*-like extreme, such a change in a series of arenesulfonates, by increasing the ease of heterolysis of the C—O bond, could also produce a shift toward the E1-like extreme (12). Thus, a study of this kind allows some evaluation of the relative importance of these two effects in determining orientation.

In the first paper in this series we reported the results of a study of the reactions of a series of 2-pentyl arenesulfonates with ethanolic sodium ethoxide. There appeared to be a very small but regular increase in the percentage of 2-pentene and in the ratio of *trans*-to *cis*-2-pentene with increasing electron withdrawal in the leaving group. However, this conclusion was clouded somewhat by the fact that, under the conditions studied, observed olefin compositions had to be corrected for competing first-order elimination. The corrections were based on two assumptions (13), neither of which could be rigorously justified.

In the present work, our aim was to minimize competition by first-order elimination by appropriate choice of base-solvent system. The compounds studied were the series of 2-methyl-3-pentyl arenesulfonates (I). This system offers an advantage over the 2-pentyl system in that E1 elimination in the solvents studied produces 15-20% of the



rearranged olefin 2-methyl-1-pentene. The presence or absence of this olefin therefore provides a test for competing first-order elimination and a non-kinetic method for correcting for competing first-order elimination, if necessary.

RESULTS

Synthesis of Starting Materials

The desired arenesulfonates were synthesized by conventional methods. All except the p-aminobenzenesulfonate Ib were prepared by treatment of 2-methyl-3-pentanol with the appropriate arenesulfonyl chloride in dry pyridine. The p-aminobenzenesulfonate was prepared by reaction of p-aminobenzenesulfonyl fluoride with sodium 2-methyl-3-pentoxide.

Product Studies

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Product studies were carried out in the four solvents: t-butanol, 50% (by volume)

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965

t-butanol – dioxane, 25% (by volume) t-butanol – dioxane, and 25% (by volume) tbutanol-dimethyl sulfoxide. All product studies, except when stated otherwise, were carried out at 50 °C. Potassium t-butoxide was the base employed in all the E2 reactions. The olefinic products were separated from the reaction mixtures by distillation and were analyzed by vapor phase chromatography.

Table I summarizes the results of the E1 product studies. The formation of the rearranged olefin 2-methyl-1-pentene indicates that at least part of the reaction involves a carbonium ion or ion pair intermediate. Direct analysis of the reaction mixture from solvolysis of Id in t-butanol showed, by the absence of any detectable t-butyl 2-methyl-3-pentyl ether, that at least 95% of the first-order reaction leads to olefinic products.

TABLE I	
Products of E1 reactions of 2-methyl-3-pentyl arenesulfonat	es

Ester	Solvent	% 2-methyl- 2-pentene	% cis-4-methyl- 2-pentene	% trans-4-methyl- 2-pentene	% 2-methyl- 1-pentene
<i>p</i> -CH₃* <i>p</i> -N(CH₃)₂*·† <i>p</i> -Br‡	<i>t</i> -Butanol 50% <i>t</i> -butanol – dioxane 50% <i>t</i> -butanol – dioxane	$77.2 \\ 65.5 \\ 71.4 \pm 0.4$	$0 \\ 1.9 \\ 0.9 \pm 0.1$	7.0 15.5 8.3 ± 0.1	$15.8 \\ 17.0 \\ 19.4 \pm 0.3$

*Single run; estimated uncertainties $\pm 0.4\%$. †Temperature = 100.0°.

[†]Temperature = 100.0° . ‡Average of three runs listed with average deviations.

The results of the E2 product studies are shown in Table II. Corrections for competing first-order elimination were made whenever 2-methyl-1-pentene was present in the olefinic products. In such cases, two sets of values are listed; the values in parentheses are uncorrected percentages based on the E2 products alone.

TABLE II Products of E2 reactions of 2-methyl-3-pentyl arenesulfonates at 50 °C* †

Ester	[Ester], M	[Base], <i>M</i>	% 2-methyl- 2-pentene	% cis-4-methyl- 2-pentene	% trans-4-methyl- 2-pentene	No. runs
$\frac{t\text{-Butanol}}{\substack{p\text{-N}(CH_3)_2\\p\text{-CH}_3}}$	$\begin{array}{c} 0.08 \\ 0.11 \end{array}$	0.48 0.48	53.3 ± 0.2 $51.1(52.6) \pm 0.3$	10.8 ± 0.1 $16.3(15.6) \pm 0.1$	35.9 ± 0.2 $32.6(31.8) \pm 0.2$	$\frac{3}{2}$
50% <i>t</i> -butanol <i>p</i> -N(CH ₃) ₂ <i>p</i> -NH ₂ <i>p</i> -OCH ₃ <i>p</i> -CH ₃ <i>p</i> -Br 3,4-di-Cl <i>p</i> -NO ₂	- dioxane 0.10 0.10 0.10 0.10 0.10 0.10 0.12, 0.09 0.10, 0.07	$\begin{array}{c} 0.47\\ 0.43\\ 0.46\\ 0.46, 0.48\\ 0.45\\ 0.48\\ 0.50, 0.67,\\ 0.41\end{array}$	$51.9\pm0.354.0\pm0.048.9\pm0.250.4\pm0.251.1(51.8)\pm0.051.1(52.5)\pm0.259.3(61.1)\pm0.6$	$\begin{array}{c} 13.4 \pm 0.1 \\ 14.9 \pm 0.1 \\ 20.6 \pm 0.2 \\ 19.3 \pm 0.2 \\ 17.8 (17.5) \pm 0.0 \\ 16.1 (15.9) \pm 0.2 \\ 9.7 (9.1) \pm 0.2 \end{array}$	$\begin{array}{c} 34.7 \pm 0.2 \\ 31.1 \pm 0.2 \\ 30.4 \pm 0.1 \\ 30.2 \pm 0.1 \\ 31.1(30.7) \pm 0.1 \\ 31.8(31.6) \pm 0.3 \\ 31.1(29.8) \pm 0.6 \end{array}$	3235336
25% <i>t</i> -butanol <i>p</i> -CH₃ <i>p</i> -Br 3,4-di-Cl	- dioxane 0.10 0.10 0.10	$0.19 \\ 0.19 \\ 0.23$	50.8 ± 0.2 52.5 ± 0.1 52.3 ± 0.4	19.0 ± 0.1 17.0 ± 0.0 15.8 ± 0.2	30.2 ± 0.1 30.5 ± 0.1 31.9 ± 0.2	3 3 3
25% <i>t</i> -butanol <i>p</i> -N(CH ₃) ₂ <i>p</i> -CH ₃ 3,4-di-Cl <i>p</i> -NO ₂ ‡	- dimethyl s 0.08, 0.10 0.10 0.07, 0.09 0.10	ulfoxide 0.18, 0.25 0.30 0.28, 0.18 0.20	$\begin{array}{c} 47.9 \pm 0.2 \\ 50.2 \pm 0.4 \\ 53.5 \pm 0.2 \\ 61(67) \pm 3 \end{array}$	2.4 ± 0.2 1.9 ± 0.1 1.3 ± 0.3 $3(3) \pm 1$	$\begin{array}{c} 49.7 \pm 0.2 \\ 47.9 \pm 0.3 \\ 45.2 \pm 0.1 \\ 36(31) \pm 3 \end{array}$	$2 \\ 3 \\ 2 \\ 1$

*Values listed with average deviations. †Values in parentheses uncorrected for competing first-order elimination, ‡Analysis made difficult by exceptionally low olefin yield (see also ref. 15).

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COLTER AND MCKELVEY: ELECTRONIC EFFECTS IN E2 REACTIONS. H

In correcting E2 product mixtures for E1 reaction, the fraction of the total olefin product arising from first-order elimination was taken as a fraction of 2-methyl-1-pentene in the mixture divided by the fraction of 2-methyl-1-pentene in the E1 product. The olefin composition from the E1 reaction of Ie in 50% t-butanol – dioxane was used in making all corrections, with the single exception of the E2 reaction of Id in t-butanol, in which case the E1 product of the same compound in t-butanol was used. The use of a single E1 product composition cannot lead to any significant error, since the E1 product mixtures are expected to be quite insensitive to leaving group and the corrections are very small.

The method of correcting for first-order elimination is based on the assumption that the carbonium ion intermediate leads to the same product mixture in the presence of base as in the absence of base. While this assumption is unlikely to be completely valid, the corrections are probably approximately correct for the following reason. In the basic media a carbonium ion is expected to yield an olefin mixture which is intermediate in composition between the E1 and E2 mixtures. Thus, while the fraction of 2-methyl-1-pentene in the basic reaction product would then underestimate the amount of competing E1 reaction, the E1 product composition used in the correction tends to make the correction too large. Most important, the corrections in all cases are much too small to change the general trends in product composition. The correction procedure is described in detail, with an example, in the Experimental section.

With the exception of the two *p*-amino esters, Ia and Ib, in *t*-butanol and 50% *t*-butanol – dioxane, the percentage of 2-methyl-2-pentene and the ratio of *trans*- to *cis*-4-methyl-2-pentene increase in a regular way with increasing electron withdrawal in the leaving group. The changes are substantial, the percentage of Saytzeff elimination increasing from 48.9% (*p*-OCH₃) to 59.3% (*p*-NO₂) in 50% *t*-butanol – dioxane and from 47.9% (*p*-N(CH₃)₂) to 61% (*p*-NO₂) in 25% *t*-butanol – dimethyl sulfoxide. The *trans* to *cis* ratio in the Hofmann olefins increases from 1.48 (*p*-OCH₃) to 3.20 (*p*-NO₂) in 50% *t*-butanol – dioxane and from 20.7 (*p*-N(CH₃)₂) to 34.8 (3,4-di-Cl) in 25% *t*-butanol – dimethyl sulfoxide. Aside from elimination of competing E1 reaction, replacement of *t*-butanol by dioxane mixtures has almost no effect on the E2 products. However, whereas the E2 reactions in 25% *t*-butanol – dimethyl sulfoxide yield a similar fraction of 2-methyl-2-pentene as the reactions in *t*-butanol and the *t*-butanol – dioxane mixtures, the ratio of *trans*- to *cis*-4-methyl-2-pentene is dramatically increased.

Rate Studies

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Substituent and solvent effects on rates of elimination could provide information about the extent of C—O bond fission and charge separation in the transition states. Consequently, second-order rate constants for reaction of selected esters with potassium *t*-butoxide were measured in *t*-butanol and 50% *t*-butanol – dioxane at 50° and in 25%*t*-butanol – dimethyl sulfoxide at 25° . The results are listed in Table III. Although certain of these reactions are known from the product studies to be accompanied by first-order reaction, no observable regular trend in calculated second-order rate constants was observed in any instance. Order of magnitude corrections for competing first-order elimination can be made where complementary product studies have been carried out. It seems safe to assume that no appreciable substitution occurs in either the first- or secondorder reaction, since it was demonstrated that at least 95% of the reaction of Id in *t*-butanol at 50° leads to olefin (see above). Therefore, the fraction of the total reaction occurring via a first-order process under the conditions of the product runs can be

1285

CANADIAN JOURNAL OF CHEMISTRY. VOL. 43, 1965

TABLE III

Second-order rate constants for reaction of 2-methyl-3-pentyl arenesulfonates with potassium *t*-butoxide

Ester	k_2 , 1 mole ⁻¹ s ⁻¹ *
<i>t</i> -Butanol, 50.06±0.02 °C <i>p</i> -Br	$9.13 \pm 0.29 \times 10^{-5}$ †
50% <i>t</i> -butanol – dioxane, <i>p</i> -N(CH ₃) ₂ <i>p</i> -OCH ₃ <i>p</i> -CH ₃ <i>p</i> -Br‡ 3,4-di-Cl§ <i>p</i> -NO ₂ ∥	$\begin{array}{c} 50.06 \pm 0.02 \ ^{\circ}\mathrm{C} \\ 5.36 \pm 0.10 \times 10^{-6} \\ 1.86 \pm 0.08 \times 10^{-5} \\ 2.81 \pm 0.20 \times 10^{-5} \\ 6.76 \pm 0.19 \times 10^{-5} \\ 2.18 \pm 0.07 \times 10^{-4} \\ 1.07 \pm 0.10 \times 10^{-3} \end{array}$
25% t-butanol – dimethy p-N(CH ₃) ₂ p-CH ₃ p-Br	l sulfoxide, 25.00 ± 0.02 °C 1.01 $\pm 0.06 \times 10^{-3}$ 1.24 $\pm 0.05 \times 10^{-2}$ 1.00 $\pm 0.04 \times 10^{-1}$
*Rate constants listed with †First-order correction would ×10 ⁻⁵ I mole ⁻¹ s ⁻¹ , ‡First-order correction ca. <u>§F</u> irst-order correction ca.	average deviations, 1 reduce this value by ca. 0.27 $0.36 \times 10^{-5} 1 \text{ mole}^{-1} \text{ s}^{-1}$, $0.06 \times 10^{-4} 1 \text{ mole}^{-1} \text{ s}^{-1}$.

||First-order correction ca. $0.15 \times 10^{-3} 1 \text{ mole}^{-1} \text{ s}^{-1}$.

estimated as already described. This value can then be used to estimate the relative magnitudes of the first- and second-order rate constant (k_1/k_2) under the conditions of the product run (13) and, if one assumes that the same ratio prevails under the conditions of the rate measurements, an approximate correction can then be applied to the observed second-order rate constant.³ Corrections for the rate constants in 50% *t*-butanol – dioxane estimated in this way are listed as footnotes to Table III. The correction for the single E2 rate in *t*-butanol was estimated as described in ref. 13 by using an approximate first-order rate constant in *t*-butanol (see below).

The rate measurements were carried out at moderately high (0.15-0.38 M) base concentrations to approximate the conditions of the product runs. The extent of aggregation of the base will, of course, be concentration dependent. Second-order behavior was assumed; however, an appreciable fraction of the reaction could depend on a higherthan-first power of the base concentration without producing noticeable trends in calculated second-order rate constants. An increase in base concentration from 0.145~Mto 0.352 M produced an increase of about 20% in the second-order rate constant for the p-N(CH₃)₂ ester (the one listed corresponds to 0.145 *M* base). This increase could be a result of elimination induced by higher aggregates of base, complex formation between the potassium ion and the amino group (see Discussion), or less specific salt effects. Further studies of the effect of base concentration on rates and products of elimination in these systems are in progress; at present, a measure of the effect of base concentration on the rates of elimination of the other arenesulfonates is not available. It is clear, however, that such effects are not large enough to affect the general nature of the results reported, and are unlikely to change appreciably the slopes of the Hammett plots (see below).

⁸Such corrections are only very approximate for two reasons. First, the method assumes that the ratio (k_1/k_2) is unaffected by the base concentration. Secondly, we must assume that the fraction of 2-methyl-1-pentene gives an accurate measure of the fraction of the reaction proceeding by first-order reaction.

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COLTER AND MCKELVEY: ELECTRONIC EFFECTS IN E2 REACTIONS. II

1287

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Hammett plots⁴ for the E2 rates in 50% *t*-butanol – dioxane at 50 °C and 25% *t*-butanol – dimethyl sulfoxide at 25 °C are shown in Figs. 2 and 3. The range of log *k* shown graphically for each point includes the uncertainty introduced by the competing first-order reaction. A least squares fit of the plot shown in Fig. 1 gives $\rho = 1.51$, a value not too different from that (1.35) obtained for the E2 reactions of 2-pentyl arenesulfonates in ethanolic sodium ethoxide at 50 °C (13). In contrast, the E2 rates in 25% *t*-butanol – dimethyl sulfoxide show an unusual sensitivity to substitution in the leaving group, ρ here being 2.40. The reactivity of the *p*-bromobenzenesulfonate relative to the *p*-toluene-sulfonate in this system (8.1) is, to our knowledge, the largest ever reported in any substitution or elimination reaction of arenesulfonates (16, 17).



FIG. 2. Hammett plot for E2 rates in 50% t-butanol - dioxane.

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FIG. 3. Hammett plot for E2 rates in 25% t-butanol - dimethyl sulfoxide.

For purposes of comparison, it would be instructive to have a measure of solvent and substituent effects for the E1 reactions of compounds I in the solvents studied. For this reason, several first-order rates were run in t-butanol and 50% t-butanol – dioxane (18). However, accurate determination of first-order rate constants was made very difficult

⁴Hammett sigma values are taken from H. H. Jaffé, Chem. Rev. 53, 191 (1953).

CANADIAN JOURNAL OF CHEMISTRY. VOL. 43, 1965

by the enormous salt effects in these nonpolar solvents (19), especially in 50% *t*-butanol – dioxane, so that first-order rate constants increase sharply with extent of reaction. From the measurements made, it can be estimated that first-order rates in *t*-butanol are faster than those in 50% *t*-butanol – dioxane by a factor of about 10. This is to be compared with a factor of 1.35 for the E2 reaction of the *p*-bromobenzenesulfonate.

Control Experiments

1288

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The stability of the olefin mixtures under the conditions of the product studies was demonstrated for all reaction media. The absence of any significant fractionation of olefins accompanying their distillation from the reaction medium was demonstrated by showing that identical olefin compositions were obtained by direct analysis of a product mixture without separation of olefins and by a method involving separation of olefins by toluene extraction. The E2 product from reaction of Id with potassium t-butoxide in 50% t-butanol – dioxane was unaffected by 0.52 M aniline. (See Discussion for the significance of this control.) The possibility that an appreciable portion of the E2 products in 25% t-butanol – dimethyl sulfoxide arises through a prior displacement of the leaving group by dimethyl sulfoxide can be ruled out on the basis of our E2 rates and rates of dimethyl sulfoxide displacements reported by Smith and Winstein (20).

DISCUSSION

With the exception of the *p*-amino esters Ia and Ib in t-butanol and 50% t-butanol – dioxane, the E2 product compositions show two important trends. First, as substitution in the leaving group is made increasingly electron withdrawing, the fraction of 2-methyl-2-pentene increases. Second, paralleling this increase in the proportion of Saytzeff elimination is an increase in the ratio of trans- to cis-4-methyl-2-pentene. Both trends are consistent with the suggestion (13) that increasing the ease of heterolysis of the C—O bond should result in a shift in the character of the transition state toward the E1-like extreme (Fig. 1). Consequently, it appears that, in the systems studied in this work, electronic influences on the ease of heterolysis of the C—O bond have a greater effect on the character of the transition state than changes in the acidities of the β -hydrogens. It must be emphasized, however, that this picture is oversimplified, since we have neglected a dimension in the spectrum of transition states. Thus, one can visualize a spectrum of synchronous transition states, for example, with little C_{β}—H and C_{α}—X bond stretching at one extreme to nearly complete bond fission at the other.

It is, of course, also possible to explain the trends in product composition in terms of changing proportions of elimination arising from two competing processes. Two such processes could be, for example, one involving a fairly synchronous E2 transition state and one involving reaction of base with an ion pair which, to account for the second-order rate law, returns to covalent ester more often that it reacts with base. The latter mechanism does not seem unreasonable for E2 reactions of secondary arenesulfonates in ethanol, t-butanol, or t-butanol – dioxane mixtures. Since competing E1 reaction occurs in most of these solvents, it seems logical to assume that the E2 transition states lean toward the E1-like extreme (11, 21).

Two features of the results deserve particular comment. The first is the dramatic difference in the character of the E2 product in 25% *t*-butanol – dimethyl sulfoxide from that in the other solvents. Although the proportion of Saytzeff elimination is similar in all solvents, elimination in the dimethyl sulfoxide containing solvent leads to remarkably high (21:1 to 35:1) ratios of *trans*- to *cis*-4-methyl-2-pentene. Equilibration of a

COLTER AND MCKELVEY: ELECTRONIC EFFECTS IN E2 REACTIONS. 11

1289

mixture containing the two olefins with potassium *t*-butoxide in dimethyl sulfoxide at 55 °C leads to a *trans* to *cis* ratio of about 6:1 (22). Thus, if one assumes a similar ratio in 25% *t*-butanol – dimethyl sulfoxide at 50 °C, the difference in the standard free energies of the activated complexes leading to *cis*- and *trans*-4-methyl-2-pentene is greater than the difference in the standard free energies of the olefins themselves. It is apparent, then, that the simple view that the proportion of Saytzeff elimination and the *trans* to *cis* ratio are both simple functions of the amount of double bond character in the transition state is incorrect, or at least not the whole story.

Several possible reasons for the abnormally high *trans* to *cis* ratio come to mind. One possibility is that the assumption of *trans* elimination through a pure symmetrical staggered transition state is incorrect. This problem is being investigated further. Whatever the reason, this result is not a general characteristic of E2 reactions in dimethyl sulfoxide. Hofmann *et al.* (23) report that reaction of 2-chlorobutane with potassium *t*-butoxide yields *trans*- and *cis*-2-butene in a ratio of 3.46:1, which is close to the equilibrium value.

The reason for the "anomalous" behavior of the p-amino compounds in t-butanol dioxane is not known, but some of the possible causes have been eliminated by control experiments. The amino groups, through more effective solvation of the potassium cation, could conceivably alter the nature of the base enough to throw the product composition out of line. This possibility was eliminated, however, by showing that the E2 product composition from Id in 50% t-butanol-dioxane in the presence of 0.52~Maniline is identical with that obtained in the absence of added aniline. It was also considered that a unimolecular cis elimination (24, 25) could be occurring in competition with the E2 reaction. To account for the anomalous E2 products, however, such a process would have to be comparable in rate to the E2 reaction. Since the absence of 2methyl-1-pentene in the base-induced reaction product indicates that the normal E1 process does not compete with the E2 reaction, the cyclic process would have to be much faster than the normal E1 process. However, the E1 product for Ia in 50% tbutanol – dioxane at 100° (Table I) is normal in every respect; hence, no other type of unimolecular reaction can be important under E2 conditions. A third possible reason for the irregular behavior of the p-amino esters is complex formation between the p-amino or p-dimethylamino group and the potassium cation. This explanation could account for the "normal" behavior of Ia in 25% t-butanol-dimethyl sulfoxide, because complex formation should occur to a much smaller extent in this solvent, since dimethyl sulfoxide is an effective cation-solvating solvent (26). If a small fraction of the substrate, say 1%, were complexed in this way and the complexed leaving group were more reactive by a factor of 100, the observed rate constant would be approximately doubled, while about 50% of the product would arise through the complexed leaving group. The E2 rate constant for Ia in 50% t-butanol – dioxane did indeed show a substantial increase with an increase in base concentration (see Results), but this may simply be a normal salt effect. A more complete study of the effect of base concentration on the E2 products is needed to answer this question. Such a study is in progress. Finally, it is possible that changes in the character of the E2 transition state brought about by substitution in a series of benzenesulfonates may be more complex than those predicted on the basis of our simple model.

EXPERIMENTAL

Preparation of Esters

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2-Methyl-3-pentanol was prepared from 2-bromopropane and propionaldehyde by a procedure similar

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965

to that of Krollpfeiffer and Seebaum (27). The crude material was fractionated and the portion boiling at 127.1 °C (at 734 mm pressure) collected. Analysis by gas chromatography showed this material to be greater than 99% pure.

Commercially available *p*-methyl-, *p*-bromo-, and *p*-nitro-benzenesulfonyl chlorides were purified as previously described (13). *p*-Aminobenzenesulfonyl fluoride and *p*-methoxybenzenesulfonyl chloride were prepared as previously described (13). Commercially available 3,4-dichlorobenzenesulfonyl chloride was purified by two fractional freezings.

p-N,N-Dimethylaminobenzenesulfonyl chloride was prepared by reaction of phosphorus pentachloride with sodium N,N-dimethylsulfanilate (28) in refluxing toluene. Dry recrystallized sodium N,N-dimethylsulfanilate (0.1 mole) and phosphorus pentachloride (0.1 mole) were refluxed in 150 ml of reagent grade toluene until the theoretical amount of hydrogen chloride was liberated (4–6 h). The reaction mixture was filtered and the filtrate washed thoroughly with aqueous sodium carbonate and water. After it was dried over magnesium sulfate, the toluene was evaporated under reduced pressure and crystallization induced by addition of pentane. The yellow crystals (70% yield) melted at 109–110 °C (lit. (29), 110°) and were not purified further.

With the exception of 2-methyl-3-pentyl *p*-aminobenzenesulfonate, the esters were prepared by reaction of the appropriate acid chloride with a stoichiometric amount of 2-methyl-3-pentanol in enough dry pyridine to effect solution. In preparing the 3,4-dichloro and *p*-nitro esters it was necessary to moderate the reaction by addition of an equal volume of dry benzene. The tightly stoppered reaction flask was left overnight in the refrigerator, after which the ester was extracted into ether and washed twice with dilute hydrochloric acid, twice with dilute aqueous sodium hydroxide, and twice with water. After it was dried over magnesium sulfate and treated with Norite A, the ether was evaporated under reduced pressure. The *p*-methyl-, *p*-bromo-, *p*-methoxy-, and 3,4-dichloro-benzenesulfonates are liquids at room temperature. The *p*-nitrobenzenesulfonate first appeared as a yellow oil but crystallized upon addition of a small amount of *n*-pentane. This ester had m.p. 51-52 °C and decomposed within a few hours at room temperature. The *p*-N,N-dimethylbenzenesulfonate was obtained as a white solid, m.p. 84-86 °C.

2-Methyl-3-pentyl p-aminobenzenesulfonate was prepared by reaction of p-aminobenzenesulfonyl fluoride with sodium 2-methyl-3-pentoxide in ether as previously described (13) for the corresponding 2-pentyl ester. The product was obtained as white plates, m.p. 99–100 °C.

Anal. Calcd. for $C_{14}H_{23}NO_3S$ (Ia): C, 58.92; H, 8.12. Found: C, 58.93; H, 8.07. Calcd. for $C_{12}H_{19}NO_3S$ (Ib): C, 56.00; H, 7.44. Found: C, 56.12; H, 7.10. Calcd. for $C_{13}H_{20}O_4S$ (Ic): C, 57.32; H, 7.40. Found: C, 57.02; H, 7.20. Calcd. for $C_{13}H_{20}O_3S$ (Id): C, 60.90; H, 7.86; S, 12.51. Found: C, 60.87; H, 8.17; S, 12.13. Calcd. for $C_{12}H_{17}BrO_3S$ (Ie): C, 44.86; H, 5.34. Found: C, 44.71; H, 5.26. Calcd. for $C_{12}H_{16}SO_3Cl_2$ (If): C, 46.31; H, 5.18. Found: C, 44.59; H, 5.18.

The *p*-nitrobenzenesulfonate (Ig) was very unstable and, for this reason, it was not possible to obtain an elemental analysis. The infrared spectrum showed strong absorption at 6.52μ , 7.41μ , and 11.68μ (characteristic of aromatic nitro) and at 7.32μ and 8.45μ (characteristic of sulfonates (30)).

Reaction Media

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t-Butanol (Fisher certified reagent grade) was distilled twice over sodium. Dimethyl sulfoxide (Fisher certified reagent grade) was distilled over calcium hydride under reduced pressure, b.p. 50 °C at 3 mm pressure, and was freshly prepared for each experiment. Dioxane was purified by Fieser's method (31). The reaction media were prepared by first dissolving, under nitrogen, clean potassium metal in an accurately known volume of *t*-butanol and then adding an accurately known volume of either dioxane or dimethyl sulfoxide. An aliquot of this mixture was then titrated with standard hydrochloric acid to determine, in moles per liter, the concentration of potassium *t*-butoxide and, hence, the amount of *t*-butanol consumed by reaction with potassium. The appropriate weight of *t*-butanol was then added to an accurately known volume of the mixture to obtain an accurately known volume ratio of the two solvents.

Product Studies

A weighed portion of ester was dissolved in 100 ml of the reaction medium in a 200-ml round-bottomed flask. The flask was swept out with nitrogen, sealed, and immersed in a constant temperature bath maintained at 50.06 ± 0.02 °C. In cases where the rate of reaction was very rapid, i.e. all reactions involving the 3,4-dichloro- and *p*-nitro-benzenesulfonates and all reactions in 25% *t*-butanol – dimethyl sulfoxide, the reaction medium was preheated to 50.06° before addition of the ester. After the reaction was calculated to be at least 99% complete, the mixture was transferred to a 500-ml round-bottomed flask containing about 350 ml of water. The olefinic materials were then concentrated by careful distillation through an 18-inch tantalumwire spiral column fitted with an ice condenser. The methylpentenes were chased through the column with a small volume of *t*-butanol – water azeotrope (b.p. 80°). Everything distilling up to 80 °C was collected.

The olefins were analyzed by vapor phase chromatography at room temperature, using helium carrier gas at a pressure of 20 p.s.i.g. and a 35-ft column packed with tricresyl phosphate (Burrell Corp., catalogue No. 341-139). The individual methylpentenes were identified by comparison of retention times with those of authentic samples.

The E2 reactions in t-butanol and t-butanol – dioxane mixtures were accompanied by precipitation of

1290

COLTER AND MCKELVEY: ELECTRONIC EFFECTS IN E2 REACTIONS. II

potassium arenesulfonate. Rate measurements showed, however, that no appreciable coprecipitation of base occurs and that no appreciable reaction occurs at the surface of the precipitate. E1 product runs always contained an excess of 2,6-lutidine to neutralize the arenesulfonic acid formed.

Correction of E2 Product Compositions

The E2 reaction of le in 50% t-butanol-dioxane will serve to illustrate the procedure for correction for competing E1 reaction. The analysis gave four peaks of area listed in the second column in Table IV. Since the pure E1 process yields 19.4% 2-methyl-1-pentene (Table I), 1.7 cm^2 represents 19.4% of all the E1 products and $1.7/0.194 = 8.76 \text{ cm}^2$ represents 100% of all the E1 products. The area of the *cis*-4methyl-2-pentene peak should then be corrected by $0.009 \times 8.76 = 0.1 \text{ cm}^2$, the area of the *trans*-4-methyl-2-pentene peak by $0.083 \times 8.76 = 0.7 \text{ cm}^2$, and the area of the 2-methyl-2-pentene peak by 0.714×8.76 $= 6.3 \text{ cm}^2$. The uncorrected and corrected areas and percentages are listed in Table IV.

TABLE IV

		Correction	of	E2	product	from	Ie i	n	50%	<i>t</i> -butanol		dioxan
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Olefin	Uncorrected area, cm ²	Uncorrected %*	Corrected area, cm ²	Corrected %
<i>cis</i> -2-Methyl-2-pentene <i>trans</i> -2-Methyl-2-pentene 2-Methyl-2-pentene 2-Methyl-1-pentene	$\begin{array}{r} 64.8 \\ 113.6 \\ 191.2 \\ 1.7 \end{array}$	$ \begin{array}{r} 17.5 \\ 30.7 \\ 51.8 \\ $	$64.7 \\ 112.9 \\ 184.9 \\ 0.0$	$17.8 \\ 31.1 \\ 51.0$

*Based on the E2 products alone.

Kinetic Studies

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In t-butanol and 50% t-butanol – dioxane, 5-ml samples of the reaction mixture were sealed in monax glass ampoules under a nitrogen atmosphere and immersed in a constant temperature bath at 50.06 \pm 0.02 °C. After thermal equilibrium, 2–3 tubes were withdrawn for the initial (zero) point. At appropriate time intervals additional tubes were withdrawn, leaving two for infinity measurements. Upon withdrawal from the bath the tubes were quenched by plunging in ice water and broken open, and the contents quantitatively transferred to a flask containing crushed ice. The mixture was then titrated with standard aqueous HCl to a phenolphthalein end point. Initial ester and base concentrations were, respectively: le in t-butanol, 0.076 M, 0.223 M; in 50% t-butanol – dioxane: Ia, 0.131 M, 0.145 M; Ic, 0.202 M, 0.323 M; Id, 0.100 M, 0.158 M; Ie, 0.103 M, 0.236 M; If, 0.314 M, 0.380 M; and Ig, 0.20 M, 0.34 M.

In 25% t-butanol – dimethyl sulfoxide, a weighed quantity of ester was dissolved in the reaction medium in a volumetric flask already immersed in a constant temperature bath maintained at 25.00 ± 0.02 °C. By using a 5-ml pipette, aliquots were transferred at appropriate time intervals to flasks containing cracked ice. The mixtures were then titrated with standard aqueous HCl using phenolphthalein indicator. Initial ester and base concentrations were, respectively: Ia, 0.100 M, 0.162 M; Id, 0.095 M, 0.162 M; and Ie, 0.106 M, 0.162 M.

Rate constants were calculated using the integrated second-order rate expression

$$k_2 t = [1/(b-a)] \ln[a(b-x)/b(a-x)],$$

where a and b are initial ester and base concentrations, respectively, and (a - x) and (b - x) are the ester and base concentrations at time t.

Control Experiments

The stability of the olefin mixtures in 50% t-butanol ~ dioxane ~ 0.47 M potassium t-butoxide at 50 °C was demonstrated by reaction of Ia for periods ranging from 33 to 90 days. Product compositions were identical within experimental uncertainty.

A 1-ml sample of olefin consisting of 90.4% cis-4-methyl-2-pentene and 9.6% trans-4-methyl-2-pentene was added to 50 ml of 25% t-butanol – dimethyl sulfoxide, 0.20 M in potassium t-butoxide. After 96 min at 50 °C (twice the longest reaction time for this medium), the olefin mixture was analyzed by the usual procedure. The composition was unchanged.

A sample of the reaction mixture from solvolysis of Id in *t*-butanol was analyzed by injecting it directly into the gas chromatograph. The analysis gave the same results, within experimental error, as those obtained by first concentrating the olefins via distillation. The spectrum showed no detectable (estimated less than 5%) *t*-butyl 2-methyl-3-pentyl ether.

In the E2 reaction of 1b in 50% *t*-butanol – dioxane, the olefins were separated from the reaction mixture by the usual distillation procedure and also by extraction with toluene. The reaction mixture from one run (100 ml) was washed three times with 10-ml portions of toluene. The toluene extract was washed Can. J. Chem. Downloaded from www.nrcresearchpress.com by SAN DIEGO STATE UNIVERSITY on 11/13/14 For personal use only.

3

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965

twice with 10-ml portions of 2 N HCl. The olefins were then concentrated by distillation. Analysis of the two olefin samples gave identical results.

The runs carried out in the presence of aniline were carried out in the usual manner, except that aniline was added to the reaction medium before addition of the ester.

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