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Reactions of 2-Pentyl Arenesulfonates with Ethanolic Sodium Ethoxide. A Study of Electronic Effects in the E2 Reaction[1,2]

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In order to evaluate the importance of electronic effects imposed by the leaving group in E2 reactions, a study of elimination in a series of 2-pentyl arenesulfonates (I) has been carried out. Second-order rate constants for reaction with sodium ethoxide in ethanol and pseudo-first-order rate constants for ethanolysis were measured for compounds I at 50°. The fractions of these reactions leading to olefinic products were determined using a procedure based on bromine addition. Compositions of olefinic products were determined by means of gas phase chromatography. Ethanolysis competes to an important extent with the second-order reactions with sodium ethoxide under the conditions studied. Appropriate corrections were therefore applied to the results of the ethanolic ethoxide experiments to obtain fractions elimination and olefin compositions for the pure second-order reactions of compounds I. As the substituent X was varied from NH_2 through NO_2 (increasing electron withdrawal) the proportion of 2-pentenes and the ratio of *trans*-2-pentene to *cis*-2-pentene in the corrected olefin compositions showed a very slight, but regular, increase. The total spread in olefin compositions is believed to be a little larger than the experimental uncertainty. The results are discussed in terms of recent views on the transition state for E2 reactions.

Introduction

Among the oldest and most useful generalizations pertaining to base-induced elimination (E2) reactions are the so-called Hofmann and Saytzeff rules.[3] In spite of the great amount of effort directed toward an understanding of E2 reactions, the theoretical basis for the Hofmann and Saytzeff rules remains a subject of controversy. The first to present a unified theory accounting for directive effects in E2 reactions were Hughes and Ingold and their co-workers.[4,5] According to the theory, the Saytzeff pattern (observed in E2 reactions of alkyl halides) is a result of domination by electromeric factors, hyperconjugative stabilization of the developing double bond in the transition state leading eventually to predominant amounts of the product containing the greatest number of alkyl groups attached to the olefinic function. The Hofmann pattern (observed in E2 reactions of onium salts) was proposed to be a result of inductive influences made dominating by the positive charge on the onium ion, resulting in abstraction of the most acidic hydrogen and leading to predominant amounts of the least alkylated olefin. In the years since their first publication on elimination reactions[6] Hughes, Ingold and their co-workers have supported their ideas with a large number of kinetic and product studies.[7]

More recently, Brown and co-workers[8] have challenged the idea that Hofmann elimination is a result of inductive influences and have suggested instead that the Hofmann rule is a manifestation of steric effects in the transition state for elimination. In one group of experiments,[8d] particularly pertinent to the present work, treatment of a series of 2-pentyl derivatives with ethanolic potassium ethoxide led to olefinic products containing the following proportions of 1-pentene: bromide (80°), 31%; iodide (80°), 30%; *p*-toluenesulfonate (80°), 48%; dimethylsulfonium iodide (80°), 87%; methyl sulfone (130°), 89%; and trimethylammonium iodide (130°), 98%. The increase in the proportion of 1-pentene in going through the series from the bromide to the trimethylammonium salt was interpreted by Brown in terms of an increase in steric requirements of the leaving group. However, inductive electron withdrawal also changes in a fairly regular way throughout the series as does the ease of heterolysis of the C–X bond.[9]

Saunders[10] has recently re-examined the olefinic products obtained on treatment of the 2-pentyl halides with ethanolic sodium ethoxide and potassium ethoxide using vapor phase chromatography. He obtained the following proportions of 1-pentene: from 2-pentyl chloride, 36.8%; from 2-pentyl bromide, 24.7%; from 2-pentyl iodide, 19.6%. The results of these experiments show a trend opposite to that which would be expected from a consideration of steric effects alone, although differences in steric requirements of the halogens should be small. The observed order is that which would be predicted on the basis of inductive effects, although Saunders prefers an explanation based on the ease of heterolysis of the carbon–halogen bond as it affects the amount of double bond character in the transition state.

In order to help evaluate the importance of electronic effects imposed by the leaving group in determining orientation in E2 reactions, a study of the reactions of a series of 2-pentyl *p*-substituted benzenesulfonates (I) in ethanolic sodium ethoxide was undertaken. In this series, substitution at the *p*-position of the benzenesulfonate leaving group does not alter steric effects near the reaction center so that any differences in the products of elimination can be attributed to electronic effects. Fur-

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[1] Sponsored by the U. S. Army Research Office (Durham).

[2] Abstracted from a thesis submitted by Richard D. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, August, 1961.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 427–448.

[4] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[5] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

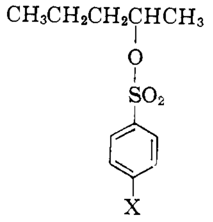
[6] W. Hanhart and C. K. Ingold, *ibid.*, 997 (1927).

[7] D. V. Banthorpe, E. D. Hughes and Sir C. K. Ingold, *ibid.*, 4054 (1960), and earlier references.

[8] (a) H. C. Brown, I. Moritani and M. Nakagawa, *J. Am. Chem. Soc.*, **78**, 2190 (1956); (b) H. C. Brown, I. Moritani and Y. Okamoto, *ibid.*, **78**, 2193 (1956); (c) H. C. Brown and M. Nakagawa, *ibid.*, **78**, 2197 (1956); (d) H. C. Brown and O. H. Wheeler, *ibid.*, **78**, 2199 (1956); (e) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956), and earlier papers in this series.

[9] C. K. Ingold, ref. 1, pp. 338–339.

[10] W. H. Saunders, Jr., S. R. Fahrenholtz and J. P. Lowe, *Tetrahedron Letters*, **18**, 1 (1960).



Ia, X = NH_2
b, X = OCH_3
c, X = CH_3
d, X = Br
e, X = NO_2

ther, the system is designed to evaluate the relative importance of inductive influences and electronic effects as they affect the ease of heterolysis of the carbon–oxygen bond, since in this series, unlike the halides, inductive electron withdrawal and ease of heterolysis parallel each other, predicting *opposite* trends in the direction of elimination.

Results

Synthesis of Starting Materials.—The desired compounds (I) were synthesized by conventional methods; Ib,c,d and e were obtained by treatment of 2-pentanol with the appropriate arenesulfonyl chloride in dry pyridine. The *p*-aminobenzenesulfonate Ia was prepared by reaction of *p*-aminobenzenesulfonyl fluoride with sodium 2-pentoxide.

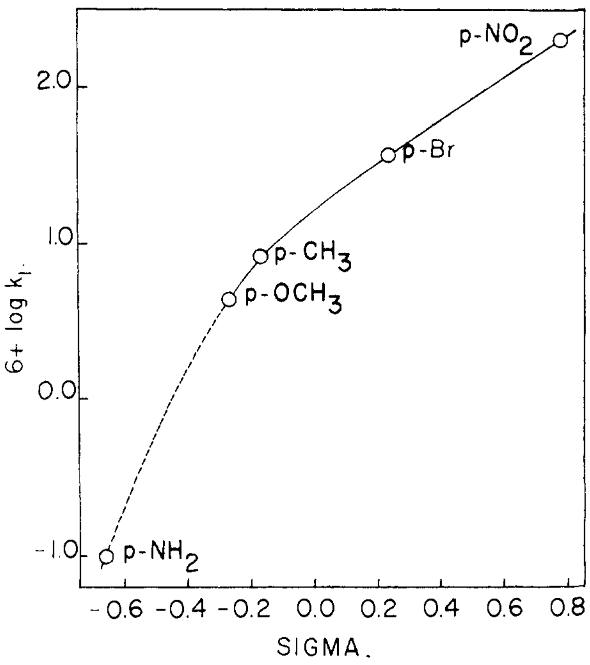


Fig. 1.—Hammett ρ–σ plot for ethanolysis of 2-pentyl arenesulfonates at 50°.

Kinetic Studies.—A kinetic study of the reaction of compounds I with ethanolic sodium ethoxide was originally undertaken to obtain some measure of the extent to which the carbon–oxygen bond is broken in the transition states for elimination, for purposes of comparison with results of similar studies, currently underway, involving other alkyl arenesulfonate series. In order to determine whether or not competing reaction with ethanol solvent was important, rates of ethanolysis in the absence of base were measured independently.

Rates of ethanolysis were measured at 50° by titration of acid at intervals of time. The resulting first-order rate constants are listed in Table I. A Hammett ρ–σ plot for the ethanolysis reaction is shown in Fig. 1. The plot shows a marked curvature, ρ varying from +2.77 for the *p*-OCH_3 to *p*-CH_3 portion of the curve to +1.34 for the *p*-Br to *p*-NO_2 portion. This finding is in line with that of Robertson[11] who measured rates of solvolysis of a series of isopropyl *m*- and *p*-substituted benzenesulfonates in absolute ethanol at 70°.

TABLE I

ETHANOLYSIS OF 2-PENTYL ARENESULFONATES AT 50°

2-Pentyl sulfonate	$10^6 k_1$, sec.$^{-1}$
p-Aminobenzene-	~0.1[a]
p-Methoxybenzene-	4.43 ± 0.06
p-Toluene-	8.28 ± .03
p-Bromobenzene-	37.4 ± .3
p-Nitrobenzene-	201 ± 4

[a] Extrapolated from ρ-σ plot (Fig. 1).

The rate constant for 2-pentyl *p*-aminobenzenesulfonate was estimated by extrapolation of the ρ–σ curve as shown in Fig. 1. Direct measurement in this case is complicated by the basic amino group which interferes with the acid-producing reaction. Though the rate constant obtained in this manner is only approximate, errors resulting from this approximation are not serious since corrections for competing ethanolysis are negligible in the reaction of Ia with ethanolic sodium ethoxide.

The kinetics of reaction of the five esters with ethanolic sodium ethoxide were measured at 50° by titration of unconsumed base at intervals of time. Second-order rate constants calculated in the usual way were corrected for the competing first-order reaction as described in the Experimental section. The corrections were largest for the *p*-nitrobenzenesulfonate and smallest for the *p*-aminobenzenesulfonate. The corrected second-order rate constants are listed in Table II. The rate constants, when used to construct a Hammett ρ-σ plot (Fig. 2) give an excellent straight line fit with ρ equal to +1.35.

TABLE II

REACTION OF 2-PENTYL ARENESULFONATES WITH SODIUM ETHOXIDE IN ETHANOL AT 50°

2-Pentyl sulfonate	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$
p-Aminobenzene-	0.467 ± 0.010
p-Methoxybenzene-	1.33 ± .06
p-Toluene-	1.86 ± .14
p-Bromobenzene-	6.97 ± .67
p-Nitrobenzene-	36.5 ± 1.1

Fraction Elimination.—The olefinic material, formed in the elimination reactions of the esters I with ethanolic sodium ethoxide at 50°, was determined by a procedure based on bromine addition. The fraction of the pure second order reaction with ethoxide leading to olefinic products (F_{2E}^0) was calculated by means of the relationship

$$F_{2E}^0 = \frac{F_E \text{ (measured)} - F_1 F_{1E}^0}{F_2}$$

where F_E (measured) is the experimentally-determined fraction elimination, F_2 is the fraction of the total reaction which occurred *via* a second-order

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[11] R. E. Robertson, *Can. J. Chem.*, 31, 589 (1953).

process, F_1 (= 1.0 − F_2) is the fraction of the reaction which was first order and $F_{1E}{}^0$ is the fraction of the first-order reaction which leads to olefinic products. The quantities F_1 and F_2 were calculated using the relationship

$$F_1 = \frac{k_1}{k_2a} \ln \frac{k_1 + k_2b}{k_1 + k_2(b - a)}$$

where k_1 and k_2 are the rate constants for the first and second-order reactions, respectively, b is the initial base concentration, a is the concentration of ester consumed and, therefore, $b - a$ is the concentration of base at the time of the olefin determination. The fraction elimination accompanying the first order reaction ($F_{1E}{}^0$) was measured for esters Id and Ie and estimated by means of a ρ–σ extrapolation for the other three esters. No significant errors are likely to be introduced by this procedure since $F_{1E}{}^0$, as expected, is relatively insensitive to the leaving group. Further, in order to produce an error in $F_{2E}{}^0$ beyond experimental uncertainty, values of $F_{1E}{}^0$ would have to be in error by an amount greater than ±2% for Ic, ±3% for Ib and ±50% for Ia. Values of $F_{1E}{}^0$ and $F_{2E}{}^0$ are listed in Table III.

TABLE III

FRACTIONS ELIMINATION

2-Pentyl sulfonate	$F_{2E}{}^0$	$F_{1E}{}^0$
p-Aminobenzene-	0.328 ± 0.010	0.065[a]
p-Methoxybenzene-	.379 ± .008	.074[a]
p-Toluene-	.369 ± .007	.077[a]
p-Bromobenzene-	.407 ± .007	.086
p-Nitrobenzene-	.370 ± .027	.099

[a] Extrapolated from a ρ-σ plot.

Although values of $F_{2E}{}^0$ do not show a completely regular trend, there seems to be a general increase in the fraction of the second-order reaction yielding olefinic products, with increasing electron withdrawal. Within the limits of experimental uncertainty this trend is very nearly regular. It is interesting to compare these results with those of Hughes and Shapiro[12] who found that in the second-order reaction of isopropyl halides with base in aqueous ethanol, the iodide gave more elimination than the bromide (60% aq. ethanol 80°) and the bromide gave more elimination than the chloride (80% aq. ethanol, 80°). Within either the halide or arenesulfonate series elimination is favored by the better leaving group.

Olefin Composition.—The olefinic products resulting by reaction of the esters I with ethanolic sodium ethoxide at 50° were separated by distillation and analyzed by vapor phase chromatography. The fraction of the over-all reaction (first order plus second order) leading to olefinic products, F_E, can be expressed as

$$F_E = F_1 \times F_{1E}{}^0 + F_2 \times F_{2E}{}^0$$

The fraction of the total olefinic product arising from the second-order process alone (F_{2E}) is given by the expression

$$F_{2E} = \frac{F_2 \times F_{2E}{}^0}{F_2 \times F_{2E}{}^0 + F_1 \times F_{1E}{}^0}$$

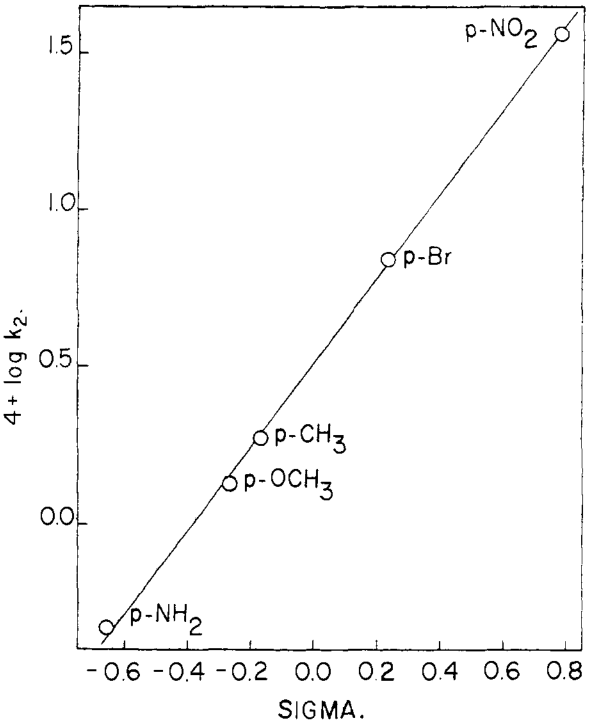

Fig. 2.—Hammett ρ–σ plot for second-order reaction of 2-pentyl arenesulfonates with sodium ethoxide in ethanol at 50°.

The observed olefin compositions were corrected to give the composition of the olefin arising from the E2 reaction alone. The correction was accomplished by subtracting out the portion arising from the first-order reaction and renormalizing the results. For example

$$F^0{}_{\text{Hofmann, 2E}} = \frac{F_{\text{Hofmann}}\,(\text{obsd.}) - F_{1E} \times F^0{}_{\text{Hofmann, 1E}}}{F_{2E}}$$

where $F^0{}_{\text{Hofmann, 2E}}$ and $F^0{}_{\text{Hofmann, 1E}}$ are the fractions of 1-pentene in the olefin mixtures from the pure E2 and E1 reactions, respectively. The corrected fractions of the Saytzeff products, *cis*- and *trans*-2-pentene, were obtained in a similar way. The corrected olefin compositions appear in Table IV.

TABLE IV

COMPOSITIONS OF E2 PRODUCTS[a]

2-Pentyl sulfonate	$F_{trans\text{-2-pentene}}$	$F_{cis\text{-2-pentene}}$	$F_{\text{1-pentene}}$
p-Aminobenzene-	0.384	0.194	0.422
p-Methoxybenzene-	.383	.193	.424
p-Toluene-	.385	.194	.421
p-Bromobenzene-	.390	.192	.418
p-Nitrobenzene-	.404	.189	.407

[a] Uncertainty for all values in the table is estimated to be approximately ±0.005.

Because of the experimental difficulties resulting from the low yields of olefin in the first-order reaction, the composition of the E1 product from the *p*-bromobenzenesulfonate Id was taken as representative of that for all of the esters. It is reasonable to expect small changes in the E1 product with changes in the leaving group, especially since $F_{1E}{}^0$ shows some dependence on leaving group. However, the correction for the first-order reaction decreases in importance in going toward the *p*-NH$_2$ end of the series. Further, for reasons discussed

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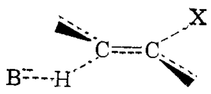
(12) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937).

below, the general nature of the results are not likely to be affected by using a common composition for the E1 product for all five esters. The E1 product from Id had the composition: 64.2% *trans*-2-pentene, 28.2% *cis*-2-pentene and 7.6% 1-pentene. From the acetolysis of 2-pentyl *p*-bromobenzenesulfonate at 70° Brown[13] obtained 48.8% *trans*-2-pentene, 35.5% *cis*-2-pentene and 15.7% 1-pentene. From the reaction of 2-pentyl *p*-toluenesulfonate with 1 *M* potassium ethoxide at 80° Brown[8d] obtained 34% *trans*-2-pentene, 18% *cis*-2-pentene and 48% 1-pentene. Although these results are in approximate agreement with ours, it appears that Brown's analyses gave consistently high results for 1-pentene. This conclusion is supported also by comparison of the results of Brown[8d] and Saunders[10] for E2 reactions of the 2-pentyl halides.

From the data listed in Table IV, the ratio of Saytzeff product to Hofmann product increases from 1.37 to 1.46 and the ratio of *trans*-2-pentene to *cis*-2-pentene increases from 1.98 to 2.14 in going through the series from Ia to Id. Before attaching any significance to these trends, it is necessary to consider whether or not they are real. The results are based not only on the gas chromatographic analyses but also on calculations involving k_1, k_2, F_{2E}^0 and F_{1E}^0. Each of these quantities has been determined experimentally and carries with it experimental error of its own. However, the gas chromatographic analyses are fairly accurate and the other quantities are used only in correction for the first-order process. As can be seen from data in the Experimental section, the effect of these corrections is to *compress* the observed trends. Consider the results for the two extreme members of the series, Ia and Ie. In the case of Ia, olefin compositions do not depend on k_1, k_2, F_{2E}^0 and F_{1E}^0 since corrections due to the competing first-order reaction are negligible. If we assume that the E1 reaction of Ie leads entirely to Saytzeff products, the calculated fraction of Hofmann product from the E2 reaction is still significantly smaller than that from Ia. However, differences between the measured compositions of olefin mixtures from Ia and Ib, Ib and Ic, and Ic and Id are well within the limits of experimental uncertainty.

Discussion

Perhaps the most significant feature of the results is the observation that the products of the E2 reaction in this series of compounds remains practically unchanged by structural changes in the leaving group resulting in a 90-fold change in reactivity. To the extent that the observed differences are real, however, they are consistent with an explanation based on the ease of heterolysis of the C–O bond as it affects the amount of double bond character in the transition state (II).[10]



II, X = O-SO$_2$-Ar

Several pieces of evidence indicate that the extent of C–H and C–X bond stretching in the transition state of E2 reactions may vary with changes in the leaving group, the solvent and the base. Evidence has come from kinetic studies of eclipsing effects in E2 reactions in the 1,2-diphenyl-1-propyl system,[14] kinetic studies of the E2 reaction of some phenyl-substituted β-phenylethyl derivatives,[15] kinetic sulfur isotope effects in E2 reactions of sulfonium salts,[16] and kinetic deuterium isotope effects in E2 reactions of some β-phenylethyl derivatives.[17]

To the extent that the transition state resembles the final product, the most stable olefin will be formed in predominant amounts. The amount of double bond character in the transition state really depends on the extent of stretching of the least stretched bond. In systems where C–H bond stretching has proceeded to a greater extent than C–O bond stretching, increasing ease of heterolysis of the C–O bond is expected to make C–H and C–O bond fission more nearly synchronous, increasing the amount of double bond character in the transition state, and therefore favoring Saytzeff elimination. Ease of C–O bond heterolysis in cases where C–O bond stretching already exceeds C–H bond stretching will probably have a similar effect on the product composition since in the limit, namely the E1 mechanism, Saytzeff products are formed in greater proportion than in any E2 reaction of the same compound.[18]

Consistent with these arguments is the observation that the ratio of *trans*-2-pentene to *cis*-2-pentene also seems to show a slight increase with increasing electron withdrawal. As the double bond character in the transition state increases, eclipsing effects are expected to become more serious, increasing the preference for formation of *trans*-2-pentene over *cis*-2-pentene.

To the extent that inductive effects are important, application of Ingold's arguments[3,8] would predict a trend opposite to that observed. The present results therefore indicate that such effects are of minor importance in E2 reactions of 2-pentyl arenesulfonates under the conditions investigated. Whether effects due to the ease of heterolysis of the C–X bond are in general more important than inductive effects in determining direction of elimination cannot be said at this time. Studies involving other solvent–base systems, other alkyl *p*-substituted benzenesulfonates and alkyl *p*-substituted sulfones are currently under way in an attempt to answer this question.

Experimental[19]

2-Pentyl Arenesulfonates.—Commercial 2-pentanol was distilled, dried, and fractionated, and the portion boiling at

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(13) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3614 (1955).

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

(15) (a) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957); (b) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957); (c) W. H. Saunders, Jr., C. B. Gibbons and R. A. Williams, *ibid.*, **80**, 4099 (1958).

(16) W. H. Saunders, Jr., and S. Asperger, *ibid.*, **79**, 1612 (1957).

(17) W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

(18) This conclusion does not necessarily predict an increase in kinetic eclipsing effects[14] with ease of C–X heterolysis since in mechanisms close to either the E1 or E1cb ends of the spectrum of mechanisms[14] product-controlling steps may involve an intermediate formed in an initial slow step.

(19) Melting points and boiling points, unless otherwise stated, are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn.

119° (cor.) collected. Subsequent analysis by gas chromatography using a diisodecyl phthalate column showed the material to be 98.99 ± 0.01% pure, $n^{20}{}_D$ 1.4068 (lit.[20] 1.4061).

Commercially available *p*-methyl-, *p*-bromo- and *p*-nitrobenzenesulfonyl chlorides were purified by washing a solution of the acid chloride in benzene, twice with saturated aqueous potassium bicarbonate and twice with water, drying over magnesium sulfate, and crystallizing from benzene–pentane. In some instances, sublimation was also used for purification. Melting points of *p*-substituted benzenesulfonyl chlorides are: *p*-bromobenzenesulfonyl chloride, 74.5–76° (lit.[21] 75°); *p*-nitrobenzenesulfonyl chloride, 78–79° (lit.[22] 80°); *p*-toluenesulfonyl chloride, 67–68° (lit.[23] 68°).

p-Methoxybenzenesulfonyl chloride was prepared from anisole and chlorosulfonic acid by the method of Morgan and Cretcher,[24] giving material melting at 41° (lit.[24] 41–42°).

With the exception of 2-pentyl sulfanilate, the esters were prepared by treatment of the appropriate acid chloride with a slight molar excess of 2-pentanol and of dried[25] pyridine at room temperature. The appropriate acid chloride was crushed with a stirring rod in the presence of 2-pentanol, and small portions of benzene added until solution was effected, at which time the pyridine was added. The resulting solution was stirred until the heat of the reaction could be felt by hand, or until the solution became cloudy, at which time the flask was tightly stoppered and placed in the refrigerator overnight.

The paste resulting from the preparation of Ib, Ic and Id was allowed to warm to room temperature and treated with 5 ml. of hot concentrated aqueous sodium hydroxide until a bright red color appeared, usually within 2 minutes. The treatment with base preferentially hydrolyzes the unreacted acid chloride in the presence of ester. The reaction with sodium hydroxide was quenched by transferring the solution to a separatory funnel containing cold 5% hydrochloric acid. The ester was extracted into ether and the combined ether extracts washed once with 5% hydrochloric acid, twice with cold saturated aqueous potassium carbonate, and twice with cold water. After drying over magnesium sulfate and treating with Norite A, the ether was evaporated off under vacuum leaving the ester as an oil. It was found that a diffusion pump was generally necessary to remove the last traces of benzene and 2-pentanol at room temperature.

2-Pentyl *p*-methoxybenzenesulfonate gave $n^{20}{}_D$ 1.5100.

Anal. Calcd. for $C_{12}H_{18}O_4S$: C, 55.79; H, 7.02; S, 12.41. Found: C, 55.74; H, 6.97; S, 12.13.

2-Pentyl *p*-toluenesulfonate gave $n^{20}{}_D$ 1.5005 (lit.[26] 1.5005).

Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.48; S, 13.23. Found: C, 59.52; H, 7.65; S, 13.15,

2-Pentyl *p*-bromobenzenesulfonate gave $n^{20}{}_D$ 1.5290 (lit.[19] 1.5313).

Anal. Calcd. for $C_{11}H_{15}BrO_3S$: C, 43.00; H, 4.92; Br, 26.01; S, 10.44. Found: C, 43.45; H, 4.97; Br, 25.70; S, 10.74.

2-Pentyl *p*-nitrobenzenesulfonate was not treated with sodium hydroxide but was simply washed as described above. White plates obtained after several crystallizations from methylene chloride–pentane melted at 63–64°.

Anal. Calcd. for $C_{11}H_{15}NO_5S$: C, 48.30; H, 5.53; N, 5.13; S, 11.73. Found: C, 48.29; H, 5.51; N, 5.21; S, 11.88.

p-Aminobenzenesulfonyl fluoride was prepared from *p*-acetamidobenzenesulfonyl chloride[27] as previously reported[28] except as modified by dioxane.[29] Thirty grams of *p*-acetamidobenzenesulfonyl chloride was boiled with 20 g. of potassium fluoride in 40 ml. of water and 50 ml. of dioxane for 2 hours. The solution was cooled, diluted with 200 ml. of water, and filtered. The solid was heated with 90 ml. of 4 *N* hydrochloric acid until solution was complete. The solution was then cooled and treated with sodium hydroxide until neutral. The resulting solid sulfanilyl fluoride, upon filtration, treatment with Norite A, and crystallization from aqueous ethanol, gave white crystals melting at 70.5–71° (lit.[28] 70°). A solution of the acid fluoride in ether was added with cooling to an equimolar quantity of sodium 2-pentoxide (slurry in ether, prepared by treatment of vigorously refluxing 2-pentanol with sodium under nitrogen) and stirred under nitrogen overnight at room temperature. Purification was effected by the same procedure described for the *p*-nitrobenzenesulfonate. 2-Pentyl sulfanilate was obtained as long white needles melting at 48.5–49.5°.

Anal. Calcd. for $C_{11}H_{17}NO_3S$: C, 54.29; H, 7.04; N, 5.76; S, 13.18. Found: C, 54.28; H, 6.88; N, 5.65; S, 13.29.

The esters were stored in the freezing compartment of the refrigerator until used.

Kinetic Measurements.—The procedure used for the kinetic measurements was essentially that of Ingold.[30] An accurately-weighed portion of ester was dissolved in a solution of sodium ethoxide in absolute ethanol in a 100-ml. volumetric flask. The resulting solutions were approximately 0.1 *N* in both reactants, the base being in slight excess. After mixing, samples of the reaction solution were transferred by means of a calibrated 5-ml. automatic pipet to partially drawn-out ampoules which were then sealed under nitrogen and immersed in a rate bath, maintained at 50.05 ± 0.02°. After 5 minutes, one tube was withdrawn for the initial "zero" point. At appropriate time intervals, additional tubes were withdrawn, saving two for infinity measurements. Upon withdrawal from the bath, the tubes were quenched by thrusting them into ice-water. The ampoules were then broken open and the contents quantitatively transferred to a flask containing 50 ml. of 95% ethanol. The resulting solutions were then titrated with standard aqueous 0.1 *N* hydrochloric acid using eight drops of standard lacmoid indicator solution.

The first-order ethanolysis rates were measured in an identical way except that no sodium ethoxide was used, and the samples were made basic by addition of a known quantity of standard aqueous sodium hydroxide to each flask before titration with standard hydrochloric acid, as described above.

The usual integrated first- and second-order rate expressions were used in the calculation of the results

$$k_1 t = \ln \frac{a}{a - x} \qquad (1)$$

$$k_2 t = \frac{1}{(a - b)} \ln \frac{b(a - x)}{a(b - x)} \qquad (2)$$

where a = initial ester concn., b = initial base concn., $(a - x)$ = ester concn. at time t, $(b - x)$ = base concn. at time t. The problem of competing first- and second-order rates has been treated previously by two different methods. Young, *et al.*,[31] have used a graphical technique which requires the evaluation of the slope in a plot of x *versus* t. Ingold, *et al.*,[32] developed eq. 3 which is exact, but for convenience the last term often is neglected to give a solution which is only approximate.

$$k_2 = k_2 \text{ (calcd. from eq. 2)} - k_1/(b - x) + t(\mathrm{d}k_2/\mathrm{d}t) \qquad (3)$$

Equation 4 can be integrated to give eq. 5, which has not previously been used to treat this problem

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - x) \qquad (4)$$

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$$k_2t = \frac{1}{a - (b + k_1/k_2)} \ln \frac{(b + k_1/k_2)(a - x)}{a(b + k_1/k_2 - x)} \quad (5)$$

Equation 5 cannot be solved explicitly for k_2, but by using the technique of successive approximations and the speed of digital computers, this equation can be used to obtain an exact solution for eq. 4. The first estimate for k_2 used on the right-hand side of eq. 5 comes from eq. 2. The new value of k_2 computed by eq. 5 is now used on the right side, the process being repeated until the successive values for k_2 agree to within some arbitrarily chosen limits, in this case, 0.1%.

A program was written in Corregate (CORREctive General Algebraic Translator Extended), the Carnegie Tech compiler language for the IBM 650. The program is also operable as 20-Gate on the high speed Bendix G-20.[33]

The rate constants listed in Table II are averages of 8 values from one run for Ia, 17 values from two runs for Ib, 11 values from two runs for Ic, 20 values from three runs for Id, and 6 values from one run for Id.

Data for one of the 2-pentyl *p*-methoxybenzenesulfonate runs are listed, for purposes of illustration, in Table V.

TABLE V

RATE DATA FOR REACTION OF 2-PENTYL *p*-METHOXYBENZENESULFONATE WITH ETHANOLIC SODIUM ETHOXIDE

Time, min.	[NaOEt][a]	[Ester][a]	Reaction, %	$10^4 k_2$, liter mole^{-1} sec.$^{-1}$	
				Uncor.	Cor.
0	0.1354	0.0787	4.47	..	
210	.1168	.0601	27.1	1.71	1.35
375	.1056	.0489	40.7	1.78	1.41
470	.1011	.0444	46.1	1.75	1.37
605	.0953	.0386	53.2	1.76	1.36
720	.0906	.0339	58.8	1.80	1.38
850	.0862	.0295	64.2	1.83	1.40
1080	.0806	.0238	71.1	1.84	1.39
1410	.0704	.0173	79.0	1.90	1.42
1715	.0701	.0134	83.7	1.91	1.40
2260	.0655	.0088	89.3	1.90	1.37
∞	.0567	.0000	100.0		
				Av.	1.39 ± 0.02

[a] Corrected for thermal expansion of ethanol.

Determination of Fraction Elimination.—Rate ampoules were withdrawn from the bath and quenched in pairs, one for bromine titration and one for titration with hydrochloric acid. It was found that unreacted Ia and Ib consumed bromine and interfered with the olefin determination. For this reason, most olefin determinations were run on infinity samples.

The method for bromine titration was patterned after that of Fritz and Hammond.[34] To a bromine flask (300-ml. erlenmeyer flask with a ground glass joint which is fitted with a funnel and vacuum take-off) was added a known excess of standard potassium bromide–potassium bromate solution. The flask was then evacuated and wrapped in aluminum foil. Bromine was generated by addition of 5 ml. of 6 *N* sulfuric acid to the funnel, then careful suction of the acid into the flask. The contents of the quenched ampoule were quantitatively transferred to a 50-ml. separatory funnel containing 25 ml. of carbon tetrachloride and washed with water to remove ethanol and sodium arenesulfonate. The carbon tetrachloride solution was transferred to a second separatory funnel where it was again washed with water and finally sucked into the bromine flask. The water layers in the two separatory funnels were extracted with a second portion of carbon tetrachloride which was added to the bromine flask. A 20-ml. portion of glacial acetic acid was sucked into the bromine flask after which it was shaken vigorously for 5 minutes. The excess bromine was converted to iodine by addition of 15 ml. of 20% potassium iodide solution, and the flask shaken for an additional 30 seconds. The vacuum was then released and the funnel carefully rinsed with water. The iodine was titrated with standard sodium thiosulfate using a starch indicator.

The fraction elimination accompanying the pure second-order reaction ($F_{2E}{}^0$) was calculated by means of eq. 6

$$F_{2E}{}^0 = \frac{F_E(\text{measured}) - F_1F_{1E}{}^0}{F_2} \quad (6)$$

where F_2 is the fraction of the total reaction which has occurred by a second-order process, F_1 (= 1.0 − F_2) is the fraction of the reaction which was first order, and $F_{1E}{}^0$ is the fraction of the first-order reaction which leads to olefinic products. The quantities F_1 and F_2 were calculated by eq. 7.

$$F_1 = \frac{k_1}{k_2a} \ln \frac{k_1 + k_2b}{k_1 + k_2(b - a)} \quad (7)$$

The derivation of this equation is as follows: At any instant during the reaction, the fraction of the reaction proceeding *via* a first-order process is given by the expression

$$F_1 = \frac{k_1(a - x)}{k_1(a - x) + k_2(a - x)(b - x)} = \frac{\text{rate of first-order process}}{\text{total reaction rate}}$$

$$= \frac{1}{1 + (k_2/k_1)(b - x)}$$

The quantity F_1 changes continuously with x so that the average fraction of the total reaction which has proceeded *via* a first order process during the interval $x = 0$ to $x = a$, can be written

$$\text{average } F_1 = \frac{\int F_1 \mathrm{d}(b - x)}{\int \mathrm{d}(b - x)} = \left. \frac{\frac{k_1}{k_2} \ln \left[1 + \frac{k_2}{k_1}(b - x) \right]}{(b - x)} \right|_{b - x = b}^{b - x = a}$$

The first-order fraction elimination ($F_{1E}{}^0$) was determined for Id and Ie only. Values of $F_{1E}{}^0$ for the other esters were obtained by extrapolation of a plot of $F_{1E}{}^0$ *versus sigma*.

The results listed in Table III are averages of 6 values for Ia, 5 values for Ib, 8 values for Ic, 11 values for Id and 9 values for Ie.

Control Experiments.—A solution of "amylene" in ethanol was prepared, and repeated analyses of aliquots of this solution gave results which were reproducible to 3 parts/1000.

Reagent grade cyclohexene was analyzed by gas chromatography and found to be 99.6% pure. Subsequent analysis of a solution of this cyclohexene of known concentration, by the bromine addition method, gave a purity of 99.2%, thus accounting for 99.6% of the known olefin content.

The presence of ethyl 2-pentyl ether was shown not to interfere with the olefin titration.

The stability of the olefinic material in the acidic first-order reaction solution was shown by determination of the fraction elimination after 10 and 20 half-lives. The two analyses gave identical results.

Olefin Compositions.—One hundred ml. of an ethanol solution, 0.1 *N* in the appropriate ester and approximately 0.2 *N* in sodium ethoxide, was prepared in a manner identical to that used for the kinetic experiments. An initial 5-ml. aliquot was withdrawn and titrated with hydrochloric acid to determine the initial base concentration, while the initial ester concentration was obtained from the measured weight of the ester. The remaining 95 ml. of solution was sealed in a 200-ml. round-bottom flask under nitrogen. After the reaction had proceeded to at least 99% of completion (calculated), the olefinic materials were concentrated by careful distillation through an 18-inch tantalum wire spiral column fitted with a Dewar Dry Ice condenser. The pentenes were chased through the column with a small portion of the ethanol and the distillate was collected in a receiver immersed in an ice-bath.

The pentenes were analyzed by gas chromatography at room temperature using a 25-foot column packed with 15% by weight of a saturated solution of silver nitrate in benzyl cyanide on 60–80 mesh Chromosorb (Fisher Scientific Co.). Peaks corresponding to the three pentenes were completely separated.

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(33) "20-Gate, Algebraic Compiler for the Bendix G-20," Computation Center, Carnegie Institute of Technology, Pittsburgh 13, Pa., July 28, 1961.

(34) J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 275.

The individual pentenes were identified by comparison of retention times with those of authentic A.P.I. isomeric pentenes.

Control Experiments.—A mixture of pentenes was analyzed, dissolved in ethanol, reseparated by the standard distillation procedure and reanalyzed. Within the experimental error (±0.5%) the mixtures gave identical analyses, showing that the distillation procedure separated the pentenes from the ethanol without fractionation of the pentenes themselves.

A mixture of pentenes was heated in the rate bath with ethanolic sodium ethoxide for a period of one week. Subsequent analysis showed no change in composition.

The uncorrected olefin compositions (base concentrations ~0.2 *N*, ester concentrations ~0.1 *N*) are listed in Table VI. The corrected olefin compositions are listed in Table IV.

TABLE VI

UNCORRECTED OLEFIN COMPOSITIONS FOR REACTION OF 0.1 *N* 2-PENTYL ARENESULFONATES WITH 0.2 *N* SODIUM ETHOXIDE IN ABSOLUTE ETHANOL

2-Pentyl sulfonate	$F_{trans\text{-}2\text{-pentene}}$	$F_{cis\text{-}2\text{-pentene}}$	$F_{1\text{-pentene}}$
p-Aminobenzene-	0.385	0.194	0.421
p-Methoxybenzene-	.394	.197	.409
p-Toluene-	.398	.199	.403
p-Bromobenzene-	.408	.199	.393
p-Nitrobenzene-	.425	.198	.377

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. X. Hydride Transfers Involving Arylcarbonium and Alkylcarbonium Ions[1]

BY N. DENO, G. SAINES AND M. SPANGLER[2]

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A linear relationship between log *k* and ΔpK_{R^+} was found by Dauben and McDonough (ref. 3) for three series of hydride transfer reactions. This same relation has now been found for the hydride transfer reaction between xanthene and a series of four triarylmethyl cations. For a given ΔpK_{R^+} value, the hydride transfer for xanthene is 10^3–10^4 faster to diarylmethyl cations than to triarylmethyl cations. For hydride transfers from aliphatic alcohols, esters and ethers to the diphenylmethyl cation, rates can be achieved in polyphosphoric acid that are at least 10^4 faster than in aqueous sulfuric acids. This effect is interpreted in terms of acidity functions. The acid-catalyzed equilibration of aliphatic alcohols and ketones has been observed. The failure of *t*-butyl alcohol to abstract hydride from xanthene in 55% H_2SO_4 is discussed.

Linear Free Energy Relations.—Dauben and McDonough[3] demonstrated that for three reaction series (triarylmethyl cations + cycloheptatriene, triarylmethyl cations + trianisylmethane and triphenylmethyl cation + triarylmethanes), each characterized by constant steric requirements at the reaction center, a plot of log *k* against ΔpK_{R^+} was linear. The symbol *k* is the rate constant and ΔpK_{R^+} is the difference in pK_{R^+} between the cation reacting and the cation forming.[4] For a given ΔpK_{R^+}, the rate of hydride transfer from cycloheptatriene to triarylmethyl cations was about 10^2 faster than for transfer between triarylmethyl systems.

The above kinetics were conducted in acetonitrile solutions using perchlorate salts of the cations. We have confirmed Dauben's relation using sulfuric acid solutions, xanthene (I) as the hydride donor and a series of four triarylmethyl cations. The data fit the linear equation $\log k = 0.76 \cdot (\Delta pK_{R^+}) - 2.86$, as shown in Table I. The rate constants for the six cations studied were invariant to at least 60% completion of the reaction and were independent of the concentrations of reactants. Triphenylmethyl cation showed no variation in *k* between 55 and 58% H_2SO_4 and 4-methoxytriphenylmethyl cation showed no variation in *k* between 45 and 50% H_2SO_4.[5]

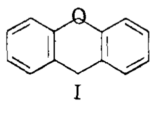

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TABLE I

RATE CONSTANTS FOR THE HYDRIDE TRANSFER REACTION BETWEEN XANTHENE AND ARYLALKYL CATIONS

Cation	Log *k* (*k* in l./mole sec.)	ΔpK_{R^+}[a]	Devn. in log *k* from correlating eq.
Triphenylmethyl	1.39	5.79	0.14
4-Methoxytriphenylmethyl	−0.907	2.56	0
4-Methyltriphenylmethyl	.593	4.40	−0.12
4,4′,4″-Trimethyltriphenylmethyl	− .807	2.72	0
4,4′-Dimethoxydiphenylmethyl	3.29	4.87	(−0.60)
1,1-Bis-(4′-methoxyphenyl)-ethyl	1.31	4.66	(−2.42)

[a] pK_{R^+} of xanthyl cation minus pK_{R^+} of the arylalkyl cation.

The linear relation between log *k* and ΔpK_{R^+} is equivalent to a linear relation between log *k* and σ^+ because ΔpK_{R^+} and σ^+ are linearly related.[6]

Steric Effects.—The steric effect of replacing one of the aryl groups on a triarylmethyl cation by first methyl and then hydrogen can be estimated from the data in Table I. Since pK_{R^+} for An_2CH^+

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[2] Research participant in the National Science Foundation program for college chemistry teachers.

[3] H. Dauben, Jr., and L. M. McDonough, Ph.D. Thesis of L. M., University of Washington, 1960.

[4] The method of evaluating pK_{R^+} is given in N. Deno, J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

[5] Experimental details appeared in the Ph.D. Thesis of G. Saines, the Pennsylvania State University, 1961. The rates were followed spectroscopically using the λ_{max} of the triarylmethyl or diarylalkyl cation.

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