# Correlation of Ethanolysis Rates of Adamantyl Arenesulfonates[1]

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**Abstract:** A recent proposal that variations in tosylate/bromide rate ratios for SN1 reactions are primarily determined by steric, rather than electronic, factors is supported by the finding that despite a rate difference of approximately $10^5$ the ethanolyses of 1-adamantyl and 2-adamantyl arenesulfonates have virtually identical responses with meta or para substitution within the leaving group. At 25.0°, the Hammett $\rho$ values are $1.76 \pm 0.08$ and $1.86 \pm 0.07$, respectively. These values are compared with others available from the literature. Contrary to what would be predicted on the basis of tabulated Hammett $\sigma$ values, the *m*-nitro derivatives react faster than the *p*-nitro derivatives. A previous suggestion that this inversion is observed as a consequence of SN2 character must be incorrect and it is shown, for solvolysis of several arenesulfonate esters of widely varying character, that deviations from "normal" behavior are due not to changes in mechanism but to the Hammett $\sigma$ values for *m*- and *p*-nitro substituents within arenesulfonates being solvent dependent. Thirteen new adamantyl arenesulfonates have been prepared and characterized.

A recent study of the effect of solvent variation upon the kinetics of solvolysis of 1-adamantyl *p*-toluenesulfonate[3] (tosylate) has been extended to a study of leaving group effects within 1- and 2-adamantyl arenesulfonates. Ethanol was chosen as the solvent for this study. In addition to studying the influence of a series of para substituents, the effect of a *m*-nitro substituent was investigated.

This investigation sheds light upon the interpretation of tosylate/bromide rate ratios, as applied to 1- and 2-adamantyl derivatives. Hoffmann[4] originally explained variations in this ratio as being due to differences in the extent of bond-breaking within the transition state; the tosylate being better able to disperse negative charge within the incipient anion was considered to be increasingly favored in terms of relative reaction rate as the extent of bond-breaking (charge-development) increased. Bingham and Schleyer[5] have argued that the variation in tosylate/bromide rate ratio between 1-adamantyl (9750 in 80% ethanol and 200,000 in acetic acid at 25°) and 2-adamantyl (231 in 80% ethanol and 16,000 in acetic acid at 25°) derivatives[6] is primarily due to relief of ground-state strain, which is especially high in the *tert*-sulfonate ester due to 1,5-nonbonded interactions involving the sulfonyl oxygen atoms.

When variations in tosylate/bromide rate ratios are due to differing degrees of charge development within the transition states, then the derivatives with the larger tosylate/bromide rate ratios should also be the more sensitive to the nature of the substitution within the arenesulfonate leaving group. On the other hand, if the variations are due primarily to differences in ground-state nonbonded interactions, with little or no difference in charge development at the transition state, then the several series of arenesulfonates should show parallel responses to meta and para substitution within the leaving group. These considerations are here applied to 1- and 2-adamantyl derivatives.

A second topic which is clarified by this investigation is the nature of the variations observed in the relative solvolysis rates of *p*- and *m*-nitrobenzenesulfonate esters. Robertson[7] studied the kinetics of solvolysis of the methyl, ethyl, and isopropyl esters in ethanol, methanol, methanol–water, and dioxane–water. Contrary to what would be expected for reactions favored by electron-withdrawing substituents,[8] the *m*-nitro derivative reacted faster than the *p*-nitro derivative for all esters in all solvents except 50% ethanol–water and 50% dioxane–water. The reversal observed for the isopropyl ester in 50% ethanol was considered to reflect an increase in ionization character within the transition state, accompanying a shift in mechanism away from SN2 and toward SN1.

If the above rationale is correct then both 1-adamantyl nitrobenzenesulfonates (nucleophilic participation prevented by the cage structure) and 2-adamantyl nitrobenzenesulfonates (nucleophilic participation considerably less than for isopropyl derivatives and possibly absent[10]) should show the faster solvolysis for the *p*-nitro compound.

Robertson's data[7] allow calculation of Hammett $\rho$ values for the ethanolyses (and other solvolyses) of methyl, ethyl, and isopropyl esters.[11] These values can be compared with those for 2-adamantyl and 1-adamantyl esters obtained in the present work. A value is also available for the ethanolyses of cyclobutyl arenesulfonates.[12]

## Results

**Ethanolyses of 1-Adamantyl Arenesulfonates.** In

(1) Abstracted, in part, from the M.S. Thesis of K. C. K., Northern Illinois University, August 1972.
(2) National Science Foundation Undergraduate Research Participant, summer 1971.
(3) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Amer. Chem. Soc.*, **92**, 7300 (1970).
(4) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).
(5) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).
(6) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).
(7) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).
(8) Hammett $\sigma$ values of +0.710 for *m*-$NO_2$ and +0.778 for *p*-$NO_2$.[9]
(9) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).
(10) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970).
(11) Several of these calculations have previously been carried out by H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
(12) D. D. Roberts, *J. Org. Chem.*, **37**, 1510 (1972).

addition to the parent 1-adamantyl benzenesulfonate, ethanolysis was carried out on the *p*-methoxy, *p*-fluoro, *p*-chloro, *p*-bromo, *p*-nitro, and *m*-nitro derivatives. Ethanolysis of the *p*-methyl derivative was reported previously.[3] Rates were determined at four or five temperatures within the range 0–55°, and all runs were carried out at least in duplicate. Constant first-order rate coefficients were obtained throughout each run. The rate data are reported within Table I and activation parameters calculated from the data are presented within Table II.

**Table I.** First-Order Rate Coefficients for Ethanolysis of 1-Adamantyl Arenesulfonates at Various Temperatures[a,b]

| Substituent | $10^5k_1$, sec$^{-1}$ 0.0° | 14.9° | 25.0° | 29.6° | 34.8° | 44.9° | 54.9° |
|---|---|---|---|---|---|---|---|
| *p*-$OCH_3$ | | 0.653 | 2.73 | | 10.3 | 38.4 | 111 |
| *p*-$CH_3$[c] | | 1.13 | 4.40 | | 14.0[d] | 54.3[e] | 138 |
| None | | 2.10 | 8.59 | | 31.8 | 110 | 354 |
| *p*-F | | 3.59 | 14.2 | | 50.5 | 173 | 522 |
| *p*-Cl | | 5.78 | 22.8 | | 84.0 | 268 | 810 |
| *p*-Br | 0.564 | 6.13 | 24.5 | | 92.4 | 321 | |
| *m*-$NO_2$ | 5.58 | 62.4 | 212 | 409 | | | |
| *p*-$NO_2$ | 4.05 | 40.8 | 149 | | 504 | | |

[a] Values are averages of two or more runs; standard error for the first-order rate coefficient associated with each run was less than 2% of its value. [b] Using Hammett $\sigma$ values from ref 9, a Hammett $\rho$ value at 25.0° of 1.76 ± 0.08 was calculated. [c] From ref 3. [d] At 35.1°. [e] At 45.9°.

**Table II.** Enthalpies ($\Delta H^{\pm}$) and Entropies ($\Delta S^{\pm}$) of Activation for Ethanolysis of 1-Adamantyl Arenesulfonates[a]

| Substituent | $\Delta H_{298}^{\pm}$, kcal/mol | $\Delta S_{298}^{\pm}$, eu |
|---|---|---|
| *p*-$OCH_3$ | 23.6 ± 0.1 | −0.3 ± 0.4 |
| *p*-$CH_3$ | 22.0 ± 0.2 | −4.7 ± 0.7 |
| None | 23.5 ± 0.1 | +1.7 ± 0.3 |
| *p*-F | 22.7 ± 0.1 | +0.1 ± 0.3 |
| *p*-Cl | 22.6 ± 0.1 | +0.7 ± 0.4 |
| *p*-Br | 23.8 ± 0.2 | +4.8 ± 0.5 |
| *m*-$NO_2$ | 23.1 ± 0.3 | +6.6 ± 0.9 |
| *p*-$NO_2$ | 22.6 ± 0.2 | +4.5 ± 0.7 |

[a] Errors quoted are standard errors.

**Ethanolyses of 2-Adamantyl Arenesulfonates.** At room temperature, these compounds undergo ethanolysis some $10^5$ times slower than the corresponding 1-adamantyl arenesulfonate. Ethanolyses of the parent compound, five para-substituted derivatives, and the *m*-nitro derivative were carried out at 55.1, 65.0, 74.8, and 85.0°. All runs were carried out at least in duplicate, and constant first-order rate coefficients were obtained throughout each run. The data, together with extrapolated logarithmic values for the rate coefficients at 25.0°, are presented in Table III, and activation parameters calculated from the data are reported in Table IV.

## Discussion

The Hammett plots for ethanolyses of 1-adamantyl and 2-adamantyl arenesulfonates at 25.0° are shown in Figures 1 and 2. For comparison, a plot constructed from Robertson's data[7] for the ethanolyses at 70° of isopropyl arenesulfonates is shown in Figure 3. It can be seen that the three plots are very similar in their features.

**Table III.** First-Order Rate Coefficients for Ethanolysis of 2-Adamantyl Arenesulfonates at Various Temperatures,[a] Extrapolated Logarithmic Values at 25.0,[b] and Hammett $\rho$ Values[c]

| Substituent | $10^5k_1$, sec$^{-1}$ 55.1° | 65.0° | 74.8° | 85.0° | Log $k_1^{25.0°}$ |
|---|---|---|---|---|---|
| *p*-$OCH_3$ | 2.73 | 11.0 | 41.1 | 139 | −9.608 ± 0.082 |
| *p*-$CH_3$ | 4.50 | 18.3 | 62.8 | 221 | −9.366 ± 0.052 |
| None | 8.34 | 33.4 | 112 | 390 | −9.085 ± 0.058 |
| *p*-Cl | 22.6 | 93.2 | 318 | 1110 | −8.673 ± 0.058 |
| *p*-Br | 25.5 | 99.9 | 346 | 1210 | −8.620 ± 0.045 |
| *m*-$NO_2$ | 223 | 905 | 2950 | 9950 | −7.624 ± 0.074 |
| *p*-$NO_2$ | 170 | 692 | 2330 | 7730 | −7.759 ± 0.074 |
| $\rho$ value | 1.81 | 1.81 | 1.79 | 1.78 | 1.86 |

[a] Values are averages of two or more runs; standard error for the first-order rate coefficient associated with each run was less than 2% (usually less than 1%) of its value. [b] Obtained as intercept (and associated standard error) of a linear least squares computer plot of log $k_1$ *vs.* $(1/T(°K) - 3.354 \times 10^{-3})$. [c] Calculated using Hammett $\sigma$ values from ref 9; standard errors of ±0.05 at the four experimental temperatures and ±0.07 at 25.0°.

**Table IV.** Enthalpies ($\Delta H^{\pm}$) and Entropies ($\Delta S^{\pm}$) of Activation for Ethanolysis of 2-Adamantyl Arenesulfonates[a]

| Substituent | $\Delta H_{298}^{\pm}$, kcal/mol | $\Delta S_{298}^{\pm}$, eu |
|---|---|---|
| *p*-$OCH_3$ | 29.9 ± 0.3 | −2.3 ± 1.1 |
| *p*-$CH_3$ | 29.6 ± 0.2 | −2.2 ± 0.6 |
| None | 29.3 ± 0.2 | −1.8 ± 0.6 |
| *p*-Cl | 29.7 ± 0.3 | +1.3 ± 0.9 |
| *p*-Br | 29.5 ± 0.2 | +1.0 ± 0.8 |
| *m*-$NO_2$ | 28.9 ± 0.2 | +3.5 ± 0.6 |
| *p*-$NO_2$ | 29.1 ± 0.2 | +3.7 ± 0.8 |

[a] Errors quoted are standard errors.

In Table V are presented Hammett $\rho$ values calculated from our data, values calculated from data available in the literature for other arenesulfonate ester solvolyses,[11] and values reported for solvolyses of cyclobutyl arenesulfonates.[12]

In ethanol, there appears to be a trend away from $\rho$ values of around +1.3 when nucleophilic participation is appreciable, through a value of +1.55 for the secondary isopropyl system, increased bond-breaking at the transition state but still appreciable nucleophilic participation,[10] to a value of around +1.8 when nucleophilic participation is absent (or, at least, extremely weak) in the 1-adamantyl, 2-adamantyl,[6,10,13–16] and cyclobutyl[12] systems.

For the cyclobutyl system, external nucleophilic participation is swamped out by internal anchimeric assistance,[12,17] and the ethanolysis rates reported[12] for cyclobutyl arenesulfonates at 60° are a little over 200 times as large as corresponding values interpolated for 2-adamantyl arenesulfonates.

Figures 1 and 2 show that in ethanol, even when nucleophilic participation is absent, the *m*-nitro derivative reacts faster than the *p*-nitro, and the suggestion[7] that inversions in the rate ratio for the two nitrobenzene-

(13) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).
(14) J. M. Harris, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 5729 (1970).
(15) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 2551 (1971).
(16) V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971).
(17) D. D. Roberts, *J. Org. Chem.*, **36**, 1913 (1971).

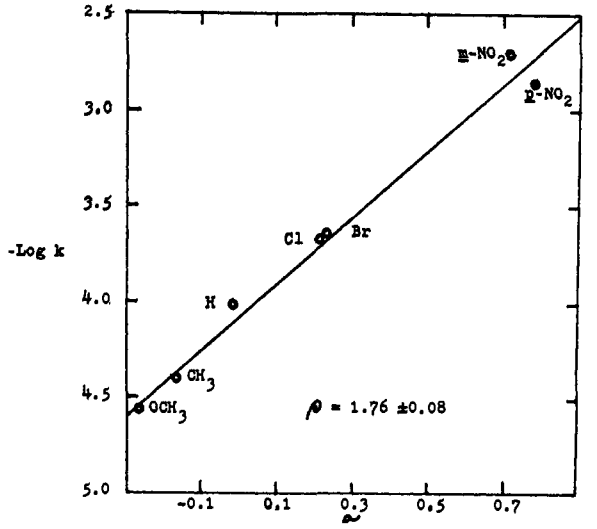


Figure 1. Hammett plot of specific ethanolysis rates of 1-adamantyl arenesulfonates at 25°.

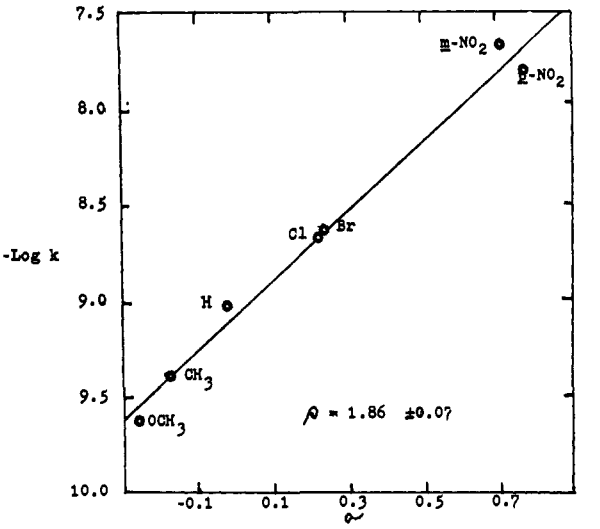


Figure 2. Hammett plot of specific ethanolysis rates of 2-adamantyl arenesulfonates at 25°.

**Table V.** Hammett $\rho$ Values for Solvolyses of Arenesulfonate Esters and Calculated Hammett $\sigma$ Values for the *m*- and *p*-Nitro Substituents

| Ester | Solvent | Temp, °C | $\rho$[a] | $\sigma_m$ | $\sigma_p$ |
|---|---|---|---|---|---|
| Me | EtOH | 70 | 1.32 ± 0.05[b,c] | 0.773 | 0.716 |
| Et | | | 1.30 ± 0.07[b,c] | 0.793 | 0.738 |
| *i*-Pr | | | 1.55 ± 0.07[b,c] | 0.781 | 0.706 |
| 2-Ad[d] | | 25 | 1.86 ± 0.07[b] | | |
| | | | 1.75 ± 0.05[e] | | |
| | | 55 | 1.81 ± 0.05[b] | 0.775 | 0.710 |
| | | 65 | 1.81 ± 0.05[b] | 0.776 | 0.711 |
| | | 75 | 1.79 ± 0.05[b] | 0.773 | 0.715 |
| | | | 1.69 ± 0.05[e] | | |
| | | 85 | 1.78 ± 0.05[b] | 0.771 | 0.710 |
| c-Bu[f] | | 50 | 1.75[e,g] | | |
| 1-Ad[d] | | 15 | 1.82 ± 0.09[b] | 0.791 | 0.690 |
| | | 25 | 1.76 ± 0.08[b] | 0.781 | 0.692 |
| | | 25 | 1.65 ± 0.07[e] | | |
| Me | MeOH | 50 | 1.25 ± 0.04[b,c] | 0.773 | 0.734 |
| *i*-Pr | | | 1.37 ± 0.07[b,c] | 0.752 | 0.733 |
| Me | 80% EtOH | 50 | 1.34 ± 0.05[b,c] | 0.751 | 0.744 |
| 2-Ad[d] | 70% EtOH | 75 | 1.64 ± 0.05[e,h] | | |
| Me | 50% EtOH | 50 | 1.25 ± 0.03[b,c] | 0.732 | 0.761 |
| *i*-Pr | | 25 | 1.57 ± 0.04[b,c] | 0.701 | 0.773 |
| | 50% Dx[i] | 50 | 1.48 ± 0.02[b,c] | 0.710 | 0.769 |
| Et | 30% EtOH | 25 | 1.18 ± 0.04[b,j] | 0.72 | 0.76 |
| c-Bu[f] | $CF_3CH_2OH$ | 25 | 1.38[e,g] | | |
| | $CH_3COOH$ | 25 | 1.43[e,g] | | |
| c-Hex[k] | | 50 | 1.40 ± 0.04[l] | 0.765 | 0.725 |
| | | 50 | 1.32 ± 0.05[e,m] | | |
| | | 75 | 1.32 ± 0.06[l] | 0.791 | 0.706 |
| | | 75 | 1.24 ± 0.03[e,m] | | |
| | | 100 | 1.19 ± 0.05[l] | 0.774 | 0.727 |
| | | 100 | 1.13 ± 0.03[e,m] | | |

[a] Errors are standard errors. [b] Including both *p*-$NO_2$ and *m*-$NO_2$. [c] Calculated from data within ref 7. [d] Ad represents adamantyl. [e] Including *p*-$NO_2$ but not *m*-$NO_2$. [f] c-Bu represents cyclobutyl. [g] From ref 12. [h] Calculated from data within J. M. Harris, J. F. Fagan, F. A. Walden, and D. C. Clark, *Tetrahedron Lett.*, 3023 (1972). [i] 50% dioxane. [j] Calculated from data within J. Demeny, *Recl. Trav. Chim. Pays-Bas*, **50**, 60 (1931). [k] c-Hex represents cyclohexyl. [l] A. R. Dahl, B.A. Thesis, Princeton University, 1966; copy of thesis kindly supplied by Professor P. v. R. Schleyer. [m] Calculated from data within footnote *l*.

sulfonate esters reflect a change in transition state structure, with the solvolysis of the para derivative favored by a shift toward SN1 mechanisms, is not supported. Indeed, in ethanol, as is shown in Table V, the same modified Hammett $\sigma$ values apply for the solvolyses of five different esters, ranging from methyl to 1-adamantyl, and for the adamantyl nitrobenzenesulfonates at several different temperatures.

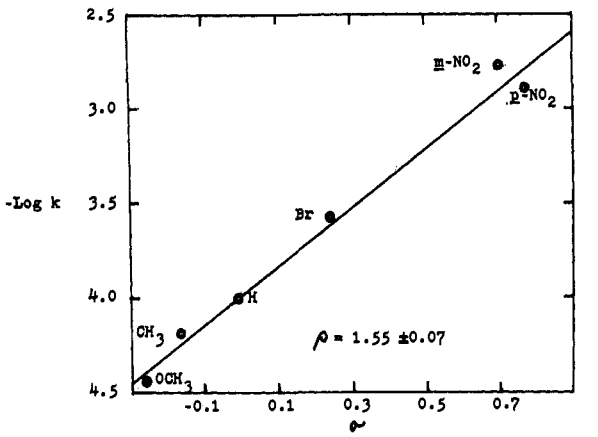


Figure 3. Hammett plot of specific ethanolysis rates of isopropyl arenesulfonates at 70°. From data of ref 7.

A survey of the modified Hammett $\sigma$ constants ($\sigma_m$ and $\sigma_p$) presented for the *m*- and *p*-nitrobenzenesulfonate solvolyses within Table V indicates that the variations in the meta/para rate ratio, superimposed upon those due to variations in reaction constant ($\rho$) values, are due primarily not to changes in mechanism[7] but to solvent effects upon the substituent constants.[18] In ethanol, the only solvent for which extensive data are available, substituent constants of +0.78 for the *m*-nitro and +0.71 for the *p*-nitro allow for excellent correlations of ethanolyses of arenesulfonate esters ranging in character from methyl esters, with extensive nucleophilic participation, to 1-adamantyl esters, with zero nucleophilic participation. While data for other solvents are less complete, there is a trend of $\sigma_m$ and $\sigma_p$ values approaching each other as the solvent is varied to methanol and then moving toward their usual values,

(18) B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, 75, 559 (1953).

with $\sigma_p$ larger, as one moves on to increasingly aqueous mixed solvents.

The $\rho$ values for the SN1 type reactions appear to decrease in value with either increased nucleophilic participation[19] or, at least for the cyclobutyl systems, with increased specific electrophilic assistance such as is present in 2,2,2-trifluoroethanol or acetic acid.[3]

For a given leaving group, the large variation in rate between the secondary and tertiary adamantyl esters is due almost entirely to an activation energy difference of 6.6 ± 1.0 kcal/mol and the entropies of activation are quite similar in value. Within either series of esters, the increase in rate with increasing electron-withdrawing power of the substituent is primarily due to an increase in the entropy of activation. The values for the entropy of activation range around zero, with electron-supplying substituents leading to somewhat negative values and electron-withdrawing substituents to somewhat positive values.[20]

The Hammett plots for 1-adamantyl and 2-adamantyl arenesulfonates have virtually identical slopes ($\rho$ values). The marginally larger value for the slower to solvolyze 2-adamantyl esters suggests that, contrary to Hoffmann's postulate,[24] their rate of solvolysis is slightly more sensitive to leaving-group effects. Due to the "abnormal" behavior of the nitrobenzenesulfonates, a more accurate assessment of the relative sensitivities to leaving-group effects is given by a direct logarithmic comparison of the specific solvolysis rates (Figure 4). This comparison, at 25.0°, gives an excellent linear plot with a calculated slope (and standard error) of 0.951 ± 0.008. The slope is very close to the unity expected if both reaction series are equally sensitive to leaving-group effects, and again the small deviation from unity suggests marginally more charge development in the transition states for the solvolyses of the 2-adamantyl esters than for the solvolyses of the 1-adamantyl esters. This observation of a virtually identical sensitivity to leaving-group effects would be consistent with the suggestion[16] that these particular SN1 reactions involve rate determining conversion of the tight ion-pair to the solvent-separated ion pair.

Bingham and Schleyer suggested[5] that variations in the tosylate/bromide rate ratio between 1- and 2-adamantyl derivatives are due not to changes in the

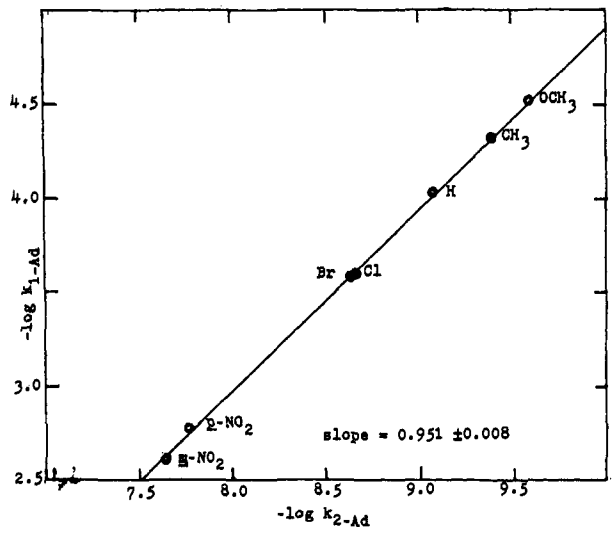


Figure 4. Logarithmic comparison of specific ethanolysis rates of 1- and 2-adamantyl arenesulfonates at 25°.

extent of charge development within the transition state but to relief of ground-state strain, which is considerably higher in the *tert*-sulfonate ester. Our present findings are consistent with this explanation and inconsistent with an explanation in terms of varying degrees of bond-breaking, which would require a slope for the logarithmic comparison of specific reaction rates (Figure 4) of in excess of unity. The small deviation from unity, despite a rate difference[26] of approximately $10^5$, confirms that SN1 (and E1) reactions do not vary very much from system to system in terms of ionic character development within the transition state,[27] and the value of slightly lower than unity indicates that insofar as there is deviation it is in the opposite direction to that required by the Hoffmann postulate[24,28] and the Swain–Thornton rule.[25] However, the Hoffmann postulate may well continue to be useful when applied to a comparison of different SN2 reactions or to a comparison of SN2 reactions with SN1 reactions.

The observation that the Hammett $\rho$ value is not very sensitive as regards the nature of the alkyl group is consistent with a previous report that, for the acetolyses of methyl, ethyl, and several secondary and bridgehead derivatives, the trifluoromethanesulfonate (triflate) to tosylate rate ratio showed little variation[30] and with a report that for the acetolysis of a series of secondary

(19) For a brief discussion, with especially emphasis on reactions of vinyl arenesulfonates, see I. Fleming and C. R. Owen, *J. Chem. Soc. B*, 1293 (1971).

(20) It now appears that the observation[21] of entropies of activation in competing solvolysis-decomposition reactions of 1-adamantyl chloroformate of some 16–20 eu more positive than corresponding values reported for solvolyses of 1-adamantyl halides[22] can be rationalized solely in terms of change in the leaving group,[23] without the need to invoke either loss of carbon dioxide concurrent with the ionization process or subsequent loss of carbon dioxide circumventing appreciable ion-pair return. For example, the value of +6.4 eu obtained[21] in ethanol is virtually indicated with the value of +6.6 eu for the ethanolysis of 1-adamantyl *m*-nitrobenzenesulfonate reported in the present study.

(21) D. N. Kevill and F. L. Weitl, *Tetrahedron Lett.*, 707 (1971).

(22) P. v. R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 2700 (1961).

(23) D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc. B*, 366 (1969).

(24) Hoffmann[4] proposed, consistent with the Swain–Thornton rule,[25] that "the faster an SN1 reaction, the more ionic its transition state." It has previously been suggested,[3] from a consideration of solvent effects upon reaction rate (*m* values), that considerably slower reacting bridgehead halides show *more* ionic character in their solvolysis transition states than *tert*-butyl chloride.

(25) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 817 (1962).

(26) A factor of $10^5$ also separates the acetolysis rates of 1- and 2-adamantyl tosylates at 25°: R. C. Fort, Jr, and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(27) A similar conclusion was reached[5] on the basis of kinetic response to solvent-ionizing power (*m* values) being virtually identical for each of a series of bridgehead bromides which varied widely in reactivity.

(28) Bingham and Schleyer[5] appear to be correct in assuming steric acceleration, considered but rejected by Hoffmann,[4] to be of prime importance in determining the nature of variations within tosylate/bromide rate ratios for SN1 reactions. However, they misrepresent the position of Hoffmann concerning the mechanism of solvolysis of simple primary and secondary substrates. Even in formic acid, Hoffmann did not assume limiting unimolecular character for solvolyses of these substrates (except for neopentyl) and the solvolyses were considered to be SN2 or mixed SN2–SN1. This is best seen in a summary presented by Ingold.[29]

(29) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 453–457 (see, especially, Table 28-5).

(30) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969).

derivatives the *p*-bromobenzenesulfonate (brosylate) to tosylate rate ratio was essentially constant.[31]

## Experimental Section[32]

**Materials.** Ethanol was purified as described previously.[3,33]

Silver salts of the arenesulfonic acids were prepared from the commercially available (Eastman) arenesulfonyl chlorides by treatment with excess silver oxide in boiling water. For example, 19 g of *p*-toluenesulfonyl chloride was dissolved in boiling water and 25 g of silver oxide was added. The mixture was vigorously stirred for about 10 min. Filtration of the hot solution and cooling of the filtrate to 0° gave white crystals which were protected from light and dried under vacuum at 80–100° for about 20 hr.

The purity of the silver salts was checked by either potentiometric titration against standardized KI solution or by the Volhard method. All of the salts were found to contain 99.5–100% of the theoretical amount of silver ion.

The 1-adamantanol and 2-adamantanol (Aldrich) were used as received. The 1-adamantanol was converted to 1-adamantyl iodide as described previously.[22,34] Pyridine was dried as described elsewhere.[35]

**1-Adamantyl Arenesulfonates.** These were prepared by the heterogeneous silver salt method, as previously reported for 1-adamantyl *p*-toluenesulfonate.[3] Several of the products, especially the *m*- and *p*-nitro esters and, to some extent, the *p*-methoxy ester, were only sparingly soluble in hexane and ether, or a hexane–ether mixture was frequently substituted. Also, with use of these solvents, the 24-hr reaction time required in hexane could be reduced to less than 2 hr. Yields were in excess of 80%.

**1-Adamantyl *p*-methoxybenzenesulfonate** was recrystallized from ether at 0°: mp 85.5–86.0°; ir includes 7.54, 7.92, 8.48, 8.58, and 14.46 μ; pmr δ 7.80 (d, 2, $J$ = 9 Hz), 6.97 (d, 2, $J$ = 9 Hz), 3.86 (s, 3, $OCH_3$), 2.16 (s, 9), 1.63 (s, 6). *Anal.* Calcd for $C_{17}H_{22}SO_4$: C, 63.33; H, 6.88; S, 9.94. Found: C, 63.2; H, 6.83; S, 10.26.

**1-Adamantyl benzenesulfonate** was recrystallized from hexane: mp 54–55°; ir includes 7.39, 7.44, 8.44, 11.00 μ; pmr[36] δ 7.88 (d, 2, $J$ = 8 Hz), 7.7–7.3 (complex, 3), 2.17 (s, 9), 1.62 (s, 6). *Anal.* Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.90; S, 10.96. Found: C, 66.0; H, 7.09; S, 11.01.

**1-Adamantyl *p*-fluorobenzenesulfonate** was recrystallized from ether: mp 96–97°; ir includes 7.51, 8.52, 8.73, 11.31, 12.03 μ; pmr[36] δ 7.91 (dd, 2, $J_{H-H}$ = 8.5 Hz, $J_{H-F}$ = 5 Hz), 7.17 (t, 2, $J_{H-H}$ = $J_{H-F}$ = 8.5 Hz), 2.18 (s, 9), 1.63 (s, 6). *Anal.* Calcd for $C_{16}H_{19}SFO_3$: C, 61.88; H, 6.17; S, 10.32; F, 6.12. Found: C, 61.8; H, 6.34; S, 10.12; F, 5.92.

**1-Adamantyl *p*-chlorobenzenesulfonate** was recrystallized from a hexane–ether mixture: mp 81.5–83.0°; ir includes 7.47, 8.51, 8.61, and 13.33 μ; pmr δ 7.85 (d, 2, $J$ = 9 Hz), 7.48 (d, 2, $J$ = 9 Hz), 2.17 (s, 9), 1.63 (s, 6). *Anal.* Calcd for $C_{16}H_{19}SClO_3$: C, 58.81; H, 5.86; S, 9.81; Cl, 10.85. Found: C, 58.8; H, 5.79; S, 9.75; Cl, 10.88.

**1-Adamantyl *p*-bromobenzenesulfonate** was recrystallized from a hexane–ether mixture: mp 94–95°; ir includes 7.53, 8.64, 13.60 μ; pmr δ 7.75 (d, 2, $J$ = 9 Hz), 7.64 (d, 2, $J$ = 9 Hz), 2.17 (s, 9), 1.63 (s, 6). *Anal.* Calcd for $C_{16}H_{19}SBrO_3$: C, 51.75; H, 5.16; S, 8.64; Br, 21.52. Found: C, 51.9; H, 5.18; S, 8.54; Br, 21.46.

**1-Adamantyl *p*-Nitrobenzenesulfonate.** Recrystallization from ether gave very pale yellow crystals: mp 112–114°; ir includes 6.59, 7.46, 8.31, 8.52, 13.57 μ; pmr 8.38 (d, 2, $J$ = 9 Hz), 8.12 (d, 2, $J$ = 9 Hz), 2.20 (s, 9), 1.65 (s, 6), *Anal.* Calcd for $C_{16}H_{19}NSO_5$: C, 56.97; H, 5.68; N, 4.15; S, 9.50. Found: C, 57.1; H, 5.97; N, 4.14; S, 9.75.

**1-Adamantyl *m*-Nitrobenzenesulfonate.** Recrystallization from ether gave very pale yellow crystals: mp 92–93°; ir includes 6.58, 7.48, 8.52, 13.68, 15.18 μ; pmr[36] δ 8.69 (s, 1), 8.46 (d, 1, $J$ = 8 Hz), 8.21 (d, 1, $J$ = 8 Hz), 7.80 (t, 1, $J$ = 8 Hz), 2.20 (s, 9), 1.66 (s, 6). *Anal.* Calcd for $C_{16}H_{19}NSO_5$: C, 56.97; H, 5.68; N, 4.15; S, 9.50. Found: C, 56.5; H, 5.98; N, 4.14; S, 9.29.

**Table VI**

A. Temp, 25.0°; 2-ml Aliquots; [1-$AdOSO_2C_6H_4$-*p*-Br], 0.0220 *M*; Titers, ml of 0.00620 *M* Methanolic NaOMe

| Time, min | 0.00 | 5.20 | 10.20 | 15.00 | 20.00 | 25.00 |
|---|---|---|---|---|---|---|
| Titer | 1.446 | 1.830 | 2.196 | 2.507 | 2.826 | 3.120 |
| $10^4k_1$, $sec^{-1}$ | | 2.38 | 2.37 | 2.34 | 2.37 | 2.38 |
| Time, min | 30.00 | 40.00 | 60.00 | | ∞ | |
| Titer | 3.422 | 3.882 | 4.711 | | 7.085 | |
| $10^4k_1$, $sec^{-1}$ | 2.43 | 2.39 | 2.44 | | | |

B. Temp, 25.0°; 5-ml Aliquots; [1-$AdOSO_2C_6H_4$-*m*-$NO_2$], 0.00391 *M*; Titers, ml of 0.00230 *M* Methanolic NaOMe

| Time, min | 0.00 | 1.00 | 2.00 | 3.00 | 4.10 | 5.00 |
|---|---|---|---|---|---|---|
| Titer | 3.038 | 3.722 | 4.239 | 4.745 | 5.172 | 5.628 |
| $10^3k_1$, $sec^{-1}$ | | 2.23 | 2.07 | 2.08 | 2.02 | 2.14 |
| Time, min | 6.00 | 7.02 | ∞ | | | |
| Titer | 5.950 | 6.243 | 8.499 | | | |
| $10^3k_1$, $sec^{-1}$ | 2.12 | 2.10 | | | | |

C. Temp, 55.1°; 5-ml Aliquots; [2-$AdOSO_2C_6H_4$-*p*-Br], 0.0537 *M*; Titers, ml of 0.00632 *M* Methanolic NaOMe

| Time, min | 0 | 2674 | 6080 | 9224 | 11987 | 15655 |
|---|---|---|---|---|---|---|
| Titer | 0.000 | 1.690 | 3.721 | 5.466 | 6.890 | 8.920 |
| $10^7k_1$, $sec^{-1}$ | | 2.53 | 2.51 | 2.49 | 2.46 | 2.51 |
| Time, min | 18643 | 20256 | 23399 | | ∞ | |
| Titer | 10.463 | 11.160 | 12.737 | | 42.47 | |
| $10^7k_1$, $sec^{-1}$ | 2.53 | 2.51 | 2.54 | | | |

D. Temp, 74.8°; 5-ml Aliquots; [2-$AdOSO_2C_6H_4$-*p*-$NO_2$], 0.0187 *M*; Titers, ml of 0.00633 *M* Methanolic NaOMe

| Time, min | 0.0 | 44.0 | 98.9 | 156.1 | 220.6 |
|---|---|---|---|---|---|
| Titer | 0.226 | 1.070 | 2.060 | 3.021 | 3.978 |
| $10^5k_1$, $sec^{-1}$ | | 2.26 | 2.27 | 2.27 | 2.25 |
| Time, min | 281.0 | 339.1 | 399.2 | 462.4 | ∞ |
| Titer | 4.887 | 5.647 | 6.350 | 7.078 | 14.81 |
| $10^5k_1$, $sec^{-1}$ | 2.28 | 2.29 | 2.27 | 2.29 | |

**2-Adamantyl Arenesulfonates.** These were prepared by the Tipson method,[37] as previously reported for 2-adamantyl *p*-toluenesulfonate.[38] The only deviation from the previously reported procedure[38] was a doubling of the reaction time. After 2 weeks at 0° (constant-temperature bath) yields were typically 70–90%.

**2-Adamantyl *p*-Methoxybenzenesulfonate.** Recrystallization at −78° gave white flakes, mp 62.7–63.2°; recrystallization at room temperature gave white square plates: mp 70.5–71.5°; ir includes 7.42, 7.89, 8.44, 8.56, 14.71 μ; pmr[39] δ 7.82 (d, 2, $J$ = 9 Hz), 6.97 (d, 2, $J$ = 9 Hz), 4.67 (s, 1, $-CH(OSO_2Ar)-$), 3.87 (s, 3, $OCH_3$), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{17}H_{22}SO_4$: C, 63.33; H, 6.88; S, 9.94. Found: C, 63.5; H, 7.00; S, 9.87.

**2-Adamantyl *p*-Toluenesulfonate.** Recrystallization at −78° gave white crystals: mp 82.1–82.5° (lit.[38] mp 82.7–83.7°); ir includes 7.52, 8.55, 11.11, 14.58 μ; pmr[39] δ 7.78 (d, 2, $J$ = 8 Hz), 7.29 (d, 2, $J$ = 8 Hz), 4.67 (s, 1, $-CH(OSO_2Ar)-$), 2.43 (s, 3, $CH_3$), 2.3–1.2 (complex, 14).

**2-Adamantyl Benzenesulfonate.** Recrystallization at −78° gave white crystals: mp 88.2–89.0°; ir includes 6.91, 7.44, 8.50, 10.90, 11.55, 12.31, 13.22, 13.90, 14.48 μ; pmr[36,39] δ 7.91 (d, 2, $J$ = 8 Hz), 7.7–7.3 (complex, 3), 4.72 (s, 1, $-CH(OSO_2Ar)-$), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.90; S, 10.97. Found: C, 65.8; H, 7.17; S, 10.82.

**2-Adamantyl *p*-Chlorobenzenesulfonate.** Recrystallization at −78° gave white crystals: mp 114.2–115.5°; ir includes 7.48, 8.47, 8.59, 10.92, 13.29, 14.89 μ; pmr[39] δ 7.83 (d, 2, $J$ = 9 Hz), 7.47 (d, 2, $J$ = 9 Hz), 4.72 (s, 1, $-CH(OSO_2Ar)-$), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{16}H_{19}SClO_3$: C, 58.81; H, 5.86; S, 9.81; Cl, 10.85. Found: C, 59.0; H, 5.97; S, 9.82; Cl, 10.96.

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**2-Adamantyl *p*-Bromobenzenesulfonate.** Recrystallization at −78° gave white crystals: mp 112.8–113.6°; ir includes 7.44, 8.54, 11.10, 13.60, 14.94 μ; pmr[39] δ 7.77 (d, 2, $J$ = 9 Hz), 7.65 (d, 2, $J$ = 9 Hz), 4.73 (s, 1, -C*H*($OSO_2Ar$)-), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{16}H_{19}SBrO_3$: C, 51.76; H, 5.16; S, 8.64; Br, 21.52. Found: C, 51.7; H, 5.08; S, 8.67; Br, 21.62.

**2-Adamantyl *p*-Nitrobenzenesulfonate.** Recrystallization at −78° gave very pale yellow crystals: mp 144–145°; ir includes 6.55, 7.37 (sh), 7.43, 8.51, 11.01, 13.56, 14.69 μ; pmr[39] δ 8.37 (d, 2, $J$ = 9 Hz), 8.13 (d, 2, $J$ = 9 Hz), 4.83 (s, 1, -C*H*($OSO_2Ar$)-), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{16}H_{19}NSO_3$: C, 56.97; H, 5.68; N, 4.15; S, 9.50. Found: C, 57.2; H, 5.81; N, 4.11; S, 9.56.

**2-Adamantyl *m*-Nitrobenzenesulfonate.** Recrystallization at −78° gave very pale yellow crystals: mp 113–114°; ir includes 6.55, 7.40, 7.45 (sh), 8.50, 11.08, 13.66, 14.99, 15.18 μ; pmr[36,39] δ 8.75 (s, 1), 8.50 (d, 1, $J$ = 8 Hz), 8.26 (d, 1, $J$ = 8 Hz), 7.80 (t, 1, $J$ = 8 Hz), 4.87 (s, 1, -C*H*($OSO_2Ar$)-), 2.3–1.2 (complex, 14). *Anal.* Calcd for $C_{16}H_{19}NSO_3$: C, 56.97; H, 5.68: N, 4.15; S, 9.50. Found: C, 57.3; H, 5.62; N, 3.97; S, 9.38.

**Kinetic Procedures.** For the ethanolysis of the 1-adamantyl arenesulfonates, the technique paralleled that previously reported[3] for the solvolysis of 1-adamantyl *p*-toluenesulfonate. The initial concentration of substrate was 0.02–0.03 $M$, except for the sparingly soluble nitro-substituted derivatives where concentrations of 0.003–0.004 $M$ were employed and 5-ml aliquots were removed from 50 ml of bulk solution, as opposed to 2-ml aliquots from 25 ml. Two illustrative runs are given in Table VI.

For the less reactive 2-adamantyl arenesulfonates higher temperatures and extended reaction times were required. The solutions, usually about 0.065 $M$ but about 0.02 $M$ for the less soluble nitro-substituted compounds, were made up at 25° and, from 50 ml of bulk solution, nine 5-ml aliquots were transferred to Kimble "neutraglas" ampoules. These ampoules were sealed, placed in the appropriate constant-temperature bath, and allowed to equilibrate, and an initial ampoule, followed by others at suitable time intervals, was removed and the contents titrated.[3] For 2-adamantyl *p*-toluenesulfonate at 85°, it was shown that variation of the initial concentration within the range 0.03–0.1 $M$ did not influence the specific ethanolysis rate. Two illustrative runs are given in Table VI. Experimental infinity titers were estimated by adding 0.5 ml of water to 1 ml of ethanol solution prior to sealing and also placing within the appropriate constant-temperature bath. Under these considerably more ionizing conditions, the solvolysis was complete within a period of less than 2 weeks. These experimental infinity titers were always within 1% of values calculated based upon the weight of 2-adamantyl arenesulfonate used within the bulk solution.

# Methylation of Anisole by Methyl-$d_3$ Chloroformate. Intermolecular Reaction of an n Complex in Electrophilic Aromatic Substitution

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**Abstract:** The methylation of anisole by methyl-$d_3$ chloroformate and silver hexafluoroantimonate in chlorobenzene gives anisole-*methyl*-$d_3$ and a mixture of unlabeled, methyl-$d_3$, and dimethyl-$d_6$ *o*-, *m*-, and *p*-methylanisoles, consistent with the principal reaction *via* initial formation of methylmethyl-$d_3$-phenyloxonium ion and its subsequent intermolecular reaction with anisole. No evidence is found for significant intermolecular rearrangement of the oxonium ion to methylanisoles under these reaction conditions. These results suggest that in electrophilic aromatic substitutions on rings bearing a substituent with a free electron pair a high yield of ortho product is not a necessary consequence of n complex formation and a low yield of ortho product is not a sufficient criterion to exclude an n complex intermediate.

Substituent effects in electrophilic aromatic substitution have been studied from several different points of view and continue to be of practical and theoretical interest. One of the probable roles for a substituent with unshared electron pairs in these reactions is participation in bond formation with the electrophile to give an n complex. It is particularly appealing to consider such species to be involved in reactions which give high yields of ortho products because intramolecular rearrangement of the complex, in most cases by a formal 1,3-sigmatropic shift, to a direct precursor of the ortho substituted compound can be readily envisioned.[2-7] In fact, n complexes are not usually considered to be reactive intermediates in electrophilic aromatic substitution unless disproportionately high yields of ortho products are observed, suggesting that the latter has become an informal criterion for the intermediacy of n complexes on the reaction pathway. We have communicated a preliminary study of the silver promoted methylation of anisole by methyl chloroformate, a reaction which

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