The Solvolysis of Arylmethyl Halides and *p*-Toluenesulfonates[1]

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Abstract: Rates of solvolysis have been measured for a number of arylmethyl halides and *p*-toluenesulfonates in dioxane–water mixtures and 80% ethanol, the aryl groups being derived from alternant hydrocarbons. Conclusions are drawn concerning the degree of nucleophilic participation by the solvent in the transition state, and on the factors influencing the efficiency of leaving groups.

Useful information concerning the mechanisms of chemical reactions can often be obtained by a combined experimental–theoretical approach, the observed relative rates for a series of analogous compounds being compared with those calculated by MO theory for various models of the transition state.

Some time ago one of us pointed out[3] the advantages of using in this connection a series of alternant hydrocarbons, or compounds of the type RX where RH is an alternant hydrocarbon. According to current theory, the atoms in alternant hydrocarbons (AH) are neutral;[4] a substituent derived from such a hydrocarbon (*e.g.*, phenyl from benzene) should therefore exert no inductive or field effects other than those due to polarity of the bond linking it to the rest of the molecule. Since the polarity of this bond will be the same for different AH substituents, any variations in rate between different molecules RX should then be due solely to mesomeric interactions involving the π electrons of the AH. These can in general be calculated more simply and more reliably than inductive or field effects; the problem of estimating relative rates is consequently much simpler than it would be for molecules of other types.

Furthermore, the MOs in AHs obey certain relationships (the so-called pairing theorem[4]) that make them particularly amenable to MO procedures; indeed, their properties can often be calculated with sufficient accuracy by a very simple method based on perturbation theory (PMO method[4]). This kind of approach has been applied successfully to a study of several reactions, in particular aromatic substitution[5] and nucleophilic aliphatic substitution.[6] In the latter case a study of the relative rates of solvolysis of a series of arylmethyl chlorides $\mathrm{ARCH_2Cl}$, ArH being an alternant hydrocarbon, gave the first unambiguous evidence for a continuity of mechanism between the extreme limiting SN1, and extreme SN2, types, as had been suggested by Winstein, Grunwald, and Jones.[7]

Here we wish to report further work on the solvolysis of analogous arylmethyl derivatives, designed to throw further light on the variation in the structure of the transition state with the polarity of the solvent and the nature of the leaving group.

Theory

Assuming the conventional localized bond model,[8] the activation energy ($\Delta E\dagger$) of a reaction can be written in the form

$$\Delta E\dagger = \Delta E\dagger_{\mathrm{deloc}} + \Delta E\dagger_{\mathrm{loc}} + \Delta E\dagger_{\mathrm{solv}} \qquad (1)$$

where $\Delta E\dagger_{\mathrm{deloc}}$, $\Delta E\dagger_{\mathrm{loc}}$, and $\Delta E\dagger_{\mathrm{solv}}$ are, respectively, the differences in bonding energy due to delocalized and localized electrons, and the difference in solvation energy, between the reactants and the transition state. In the case of a series of related reactions, the change in the number and types of localized bonds in passing from the reactants to the transition state is the same; any differences in the term $\Delta E\dagger_{\mathrm{loc}}$ are therefore small second-order effects, due to differences in hybridization, etc. If these second-order effects are neglected, and if it is assumed that the terms $\Delta E\dagger_{\mathrm{solv}}$ are the same along our series of related reactions, eq 1 can be written

$$\Delta E\dagger = A + \Delta E\dagger_{\mathrm{deloc}} \qquad (2)$$

where A is a constant. If we are also prepared to assume that the entropies of activation are the same throughout,[4,6b] then the rate constants k for the individual reactions will be given by the expression

$$-RT \log k = B + \Delta E\dagger_{\mathrm{deloc}} \qquad (3)$$

where B is another constant. The *delocalization energies of activation* ($\Delta E\dagger_{\mathrm{deloc}}$) can be calculated by some appropriate MO procedure for various models of the transition state; comparison of these with the experimental values for k, using eq 3, may then enable us to distinguish between the various models.

Dewar and Sampson[6] applied this procedure to the solvolysis of arylmethyl chlorides in various solvents, using the PMO method to estimate $\Delta E\dagger_{\mathrm{deloc}}$. They showed that for the transition state of Figure 1, S being the attacking nucleophile

$$\Delta E\dagger_{\mathrm{deloc}} \simeq C - a_{\mathrm{or}}[(\beta^2_{\mathrm{CCl}} + \beta^2_{\mathrm{CS}})^{1/2} + \beta_{\mathrm{CC}}] \qquad (4)$$

where C is a constant, a_{or} is the nonbonding MO (NBMO) coefficient at the methylene carbon in the odd AH $Ar\mathrm{CH_2}$, β_{CCl} and β_{CS} are the resonance in-

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[1] This work was supported by the Air Force Office of Scientific Research through Grant Number AF-AFOSR-1050-67.

[2] N.A.S.A. Trainee, 1965–1968.

[3] See M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 69 (1964).

[4] See M. J. S. Dewar, *J. Amer. Chem. Soc.*, 74, 3341, 345, 3350, 3353, 3355, 3357 (1952); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

[5] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[6] (a) M. J. S. Dewar and R. J. Sampson, *ibid.*, 2789 (1956); (b) *ibid.*, 2946 (1957); (c) *ibid.*, 2952 (1957).

[7] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951).

[8] See M. J. S. Dewar, *Chem. Eng. News*, **43**, 86 (1965); *Tetrahedron Suppl.*, **8**, 75 (1966).

tegrals for the CCl and CS bonds in the transition state, and β_{CC} that for the *Ar*-CH$_2$ bond, in ArCH$_2$. If the transition states for solvolysis in a given solvent have similar structures, so that β_{CCl} and β_{CS} have constant values, eq 4 can be written

$$\Delta E\dagger_{deloc} = C - a_{or}D \qquad (5)$$

where D is another constant. From eq 3-5, log k should then be a linear function of a_{or}, with slope equal to

$$\frac{(\beta^2{}_{Cl} + \beta^2{}_{CS})^{1/2} + \beta_{CC}}{RT} \qquad (6)$$

Since β_{CC} is negative, and numerically greater than the square root, the slope of the plot should be negative, and its numerical magnitude should be greater, the smaller β_{CCl} and β_{CS}. Thus the maximum slope should be observed in limiting SN1 reactions, where the transition state is essentially an ion pair (*Ar*CH$_2{}^+$, Cl$^-$) and $\beta_{CCl} = \beta_{CS} = 0$; the slope should become progressively less, the greater the degree of nucleophilic participation by the solvent in the transition state.

The observed rates of solvolysis followed this relation.[6] The maximum slope was observed for formolysis, formic acid being a poor nucleophile but a good ionizing solvent. The slopes decreased with increasing nucleophilicity of the medium, the minimum value being observed for the "pure SN2" reaction of the chlorides with iodide ion in dry acetone. The slope of a given plot can therefore be taken as a measure of the degree of nucleophilic participation, *i.e.*, of covalent binding of the entering nucleophile and the leaving group in the transition state.

Equations 5 and 6 also imply that there should be linear free energy relations between the rates of reaction of a given series of chlorides ArCH$_2$Cl, and each of a series of nucleophiles S$_1$, S$_2$, etc. Correlations of this kind have been pointed out by Streitwieser.[9]

The earlier PMO treatment[6] led to an apparent distinction between chlorides with both positions *ortho* to CH$_2$Cl free (*e.g.*, β-chloromethylnapthalene), and those with one position blocked (*e.g.*, α-chloromethylnaphthalene). The plots of eq 5 were linear for compounds of the same type, but the two lines, while parallel, were not coincident. Dewar and Sampson attributed this to steric hindrance in the ions of α-naphthylmethyl type, an explanation used by Streitwieser to account for a similar apparent distinction between α-naphthyl and β-naphthyl types in the deprotonation of arylmethanes by base.[10] However, later calculations of the term $\Delta E\dagger_{deloc}$ in eq 3, using an SCF-MO approach, gave a single line for the plot of log k *vs.* $\Delta E\dagger_{deloc}$,[11] suggesting that the earlier "steric effect" was an artifact of the admittedly rather crude method used to estimate $\Delta E\dagger_{deloc}$. This conclusion has been further supported by Gleicher,[12] who has shown that introduction of an allowance for strain effects due to the *peri* hydrogen actually impairs the correlation between log k and the SCF-MO value for $\Delta E\dagger_{deloc}$. Strain effects of this kind are undoubtedly important in the 2-aryl-2-chloropropanes, where the α-naphthyl derivative solvolyses more slowly than the β-naphthyl isomer;[6c] the group $-{}^+$CMe$_2$ is of course much larger, and more liable to hindrance, than $-{}^+$CH$_2$.

However even with values for $\Delta E\dagger_{deloc}$ calculated by the SCF-MO method, the plots of log k *vs.* $\Delta E\dagger_{deloc}$ show considerable scatter, and this becomes worse, the more nucleophilic the solvent.[4] It seems very likely that this is due to variations in the heat of solvation of the nascent ions ArCH$_2{}^+$; for whereas a plot of pK_A *vs.* $\Delta E\dagger_{deloc}$ for the protonation of aromatic hydrocarbons gives a good straight line,[4] a corresponding plot for equilibria of the type

$$Ph_3COH \rightleftharpoons Ph_3C^+ + OH^-$$

is very scattered.[13] In the former case the pK_A were measured in strong sulfuric acid; in the latter the measurements were mostly made in more nucleophilic solvents such as water or ethanol.

If so, the effects of solvent could be at least partly allowed for by using a plot of the type suggested by Streitwieser,[6] in which log k is plotted not against $\Delta E\dagger_{deloc}$ but against log k for a standard reaction in a standard solvent. For this purpose solvolysis of arylmethyl chlorides in 80% aqueous ethanol is probably as good a choice as any,[9] being reasonably nucleophilic and having the further advantage that extensive measurements have been reported. We will refer to plots of this kind as *Streitwieser plots*.

Experimental Section

Solvents. Distilled water was purified by passage through an ion exchange column (Illco Way, Research Model) and stored under nitrogen.

1,4-Dioxane (J. T. Baker, Reagent Grade) was passed through a column of neutral alumina, refluxed over sodium for several hours, and finally distilled through a 3-ft Vigreux column, bp 100-101°. The 79.5, 70, and 60% (by volume) aqueous dioxane solutions were prepared gravimetrically and stored under nitrogen.

Ethanol was purified by the method recommended by Vogel;[14] aqueous ethanol (80% by volume) was prepared according to Winstein, Grunwald, and Jones[6a] and stored under nitrogen.

Materials. The preparation of the various arylmethyl derivatives will be described in a later paper where their nmr spectra are discussed. All the new compounds gave satisfactory analyses, etc., while the physical properties of known ones corresponded to those reported in the literature.

Kinetic Methods. The kinetic data were obtained by the various methods described below. All of the kinetic runs were followed through at least 50% completion, and in most cases through greater than 70% reaction. All obeyed the first-order rate law and the data were fitted to the usual first-order rate expression, using a CDC 6600 digital computer and a least-squares program written by Mr. J. Hashmall. Kinetic runs were performed in duplicate and agreed within 3% of the mean value.

The rates of solvolysis of the arylmethyl tosylates in the various dioxane-water mixtures were measured conductometrically, the cell being similar to that described by Jones, Squires, and Lynn,[15] apart from having bright platinum electrodes. In a typical experiment, the arylmethyl tosylate was weighed into the detachable side arm of the cell. Solvent was then pipetted into the cell and the side arm replaced. After temperature equilibration, the cell was tilted so that the tosylate dissolved giving a *ca.* 10^{-4} *M* solution. Conductance measurements were then taken at timed intervals using an Industrial Instruments RC18 AC conductance bridge at 1 kHz.

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(9) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961.

(10) A. Streitwieser and W. C. Langworthy, *J. Amer. Chem. Soc.*, **85**, 1757 (1963).

(11) M. J. S. Dewar and C. C. Thompson, Jr., *ibid.*, **87**, 4414 (1965).

(12) G. J. Gleicher, *ibid.*, **90**, 3397 (1968).

(13) M. J. S. Dewar and A. Harget, unpublished work.

(14) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green & Co., Ltd., London, 1956.

(15) W. M. Jones, T. G. Squires, and M. Lynn, *J. Amer. Chem. Soc.*, **89**, 318 (1967).

Table I. Rate Constants for the Solvolysis of Arylmethyl *p*-Toluenesulfonates, and Ionization Energies Calculated by an SCF–MO Method

Aryl group	First-order rate constant ($\times 10^{-4}$ sec^{-1}) 79.5% aqueous dioxane at 40°	 70% aqueous dioxane at 40°	 60% aqueous dioxane at 30°	 Acetic acid[a] at 40°	ΔE, eV[b]
Phenyl	0.74	2.80	3.03	0.17	(0)
2-Naphthyl	3.68	12.6	12.3	2.3	−0.311
2-Phenanthryl	4.17	12.4	13.7	2.6	−0.439
3-Phenanthryl	8.32	31.3	40.2	9.1	−0.500
9-Phenanthryl	13.6	51.5	80.7	20.0	−0.614
1-Naphthyl	16.2	61.7	105	17	−0.477
1-Anthryl	108				−0.757

[a] Reference, 9, p 370. [b] Calculated[13] difference in energy between $ArCH_2OTs$ and $ArCH_2^+$, relative to value for benzyl.

An infinity reading was taken after the conductance became constant, usually 8–10 half-lives. Since it had been established that the conductance was proportional to concentration over the range used in the kinetic runs, the conductance was used directly in the first-order rate equation. Experimental infinity values generally agreed to within 3% with the theoretical value obtained from the conductance–concentration plot.

Rates of solvolysis of the bromides and chlorides in dioxane–water were measured by the titrimetric method of Dewar and Sampson.[5] The arylmethyl halide was weighed accurately into a 50-ml volumetric flask and solvent was then added to the mark. Aliquots (4–5 ml) were sealed in ampoules and immersed in a thermostat. Ampoules were removed at timed intervals, quenched at 0°, and opened, and the contents diluted with acetone (20 ml) and titrated with triethylamine in toluene (0.0102 *N*) using lacmoid as indicator. That this titration was not complicated by the possible side reaction of triethylamine with arylmethyl halides was shown by the stability of the end points and the fact that the zero time titrations gave one-drop end points. After ten half-lives, a tube was removed for the infinity titration.

Attempts to measure the kinetics of solvolysis of the arylmethyl iodides in dioxane–water failed. The solutions became dark orange, the infinity values were very low, and the kinetic plots were nonlinear. Free radical processes were no doubt responsible for this behavior; attempts to improve the situation by careful degassing did not alter the situation. Since the problem was thought to be due to the presence of residual traces of peroxide in the dioxane, measurements were then made in 80% ethanol; here reproducible rates were obtained (see below).

The solubilities of the arylmethyl tosylates in 80% ethanol, with the exception of benzyl tosylate, were not sufficient for kinetic measurements; therefore only the arylmethyl halides were studied in this solvent. The rates of solvolysis of benzyl bromide and 2-naphthylmethyl bromide were measured using the titrimetric technique described above. The rates of solvolysis of the remaining arylmethyl bromides were studied conductometrically. The concentration–conductance relation for HBr in 80% ethanol was found to be linear over the limited concentration range (0–3.5 × 10^{-4} *M*) used here. As a check, the rate of solvolysis of 1-naphthylmethyl bromide was measured using both the titrimetric and the conductometric methods; the results agreed closely. In the case of the phenanthrylmethyl bromides, a problem arose. These compounds dissolved so slowly that initial curvature was observed in the rate plots. The difficulty was circumvented by using the following technique. The arylmethyl bromide was weighed and placed in the main body of the conductivity cell along with dry ethanol (8 ml). Pure water (2.0 ml) was placed in the side arm and the entire system was thermostated. At zero time, the contents of the two compartments were mixed, giving a solution of the arylmethyl bromide in 80% ethanol. That no significant amount of ethanolysis of the tosylates had occurred during equilibration was indicated by the initial low conductance of the solution formed upon mixing. Comparison with the usual conductometric technique was made by measuring the rate of solvolysis of 1-naphthylmethyl bromide by both methods; the results agreed closely.

The rates of solvolysis of the arylmethyl iodides in 80% ethanol were measured by the same titrimetric technique as for the bromides. Here, however, the ampoules containing the kinetic aliquots were degassed at 0.05 mm by the usual freeze–thaw technique and sealed at this pressure. Unlike the results in dioxane–water, the iodides gave clean first-order kinetics in the degassed solution and the infinity titers agreed within several per cent of the theoretical. Only slight yellow colors developed over the course of the reactions.

Since the kinetic data obtained here for the arylmethyl bromides and iodides in 80% ethanol were to be compared with data obtained by Sampson and Dewar[6] for the chlorides under identical conditions, one further check was made to ensure that solvent, temperature, etc. were the same in both studies. The rate of solvolysis of 1-chloromethylnaphthalene in 80% ethanol at 50° was measured by the titrimetric method and found to be identical with the earlier[6] value.

Results and Discussion

Our first objective was to see how the structure of the transition state is affected by the concentration of water in mixed solvents. It is of course well known that the rates of S_N1 solvolysis in solvents such as aqueous dioxane increase greatly with increasing water concentration; this would normally be attributed to increasing stabilization by solvation of the ionic intermediates and to a consequent increase in ionic character of the transition state. However Streitwieser plots[9] of log *k* for solvolysis of arylmethyl chlorides $ArCH_2Cl$, ArH being an alternant hydrocarbon, in 50.7 and 79.5% aqueous dioxane had almost identical slopes (0.7 and 0.6, respectively), implying that the transition states are similar, in spite of the fact that the reactions in the former solvent were about a hundredfold faster. Measurements were, however, available for only four compounds, and the rates of three of these were very similar; we therefore decided to reinvestigate the matter. Table I shows rates of solvolysis of a number of arylmethyl tosylates in 60, 70, and 79.5% aqueous dioxane; unfortunately the esters would not dissolve in more aqueous mixtures, while the conductometric method used to measure the rates failed in solutions containing less than 20% water.

Figure 1 shows Streitwieser plots of log *k* for solvolysis in water–dioxane mixtures against log *k* for solvolysis in 80% aqueous ethanol at 50°. It will be seen that the slopes of the lines are indeed very similar, although the rates of solvolysis of a given ester again vary by a factor of about 100 over the series of solvents.[16] Apparently the increase in rate is not accompanied by any significant change in the structure of the transition state.

Figure 1 also shows a similar plot[9] for the solvolysis of the arylmethyl tosylates in acetic acid at 40°. Here the slope of the line is much greater than for the aqueous dioxane reactions, indicating that the transition state in

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(16) Note that the measurements in 60% aqueous dioxane were made at a lower temperature; the rates in this solvent were too fast to be measured at 40°.

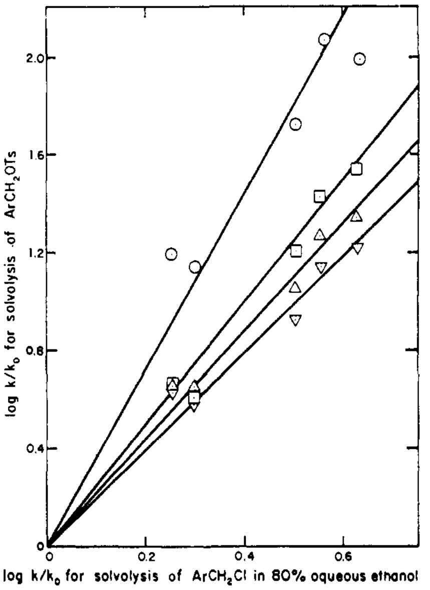

Figure 1. Plots of log (relative rate) for solvolysis of $ArCH_2Cl$ ($PhCH_2Cl$ = 1) in 80% aqueous ethanol at 50° *vs.* log (relative rate) for solvolysis of $ArCH_2OTs$ ($PhCH_2OTs$ = 1) in (a) acetic acid at 40° (⊙); (b) aqueous dioxane containing 60% (⊡), 70% (△), and 79.5% (▽) dioxane, at 30, 40, and 40°, respectively.

acetic acid has much more carbonium ion character; yet the reactions in acetic acid are generally slower than those in even the least aqueous dioxane mixture at the same temperature.

The last column of Table I shows relative energy differences (ΔE) calculated[17] by an improved version of the earlier SCF-MO procedure[11] for the process

$$ArCH_2X \longrightarrow ArCH_2^+ + X^- \qquad (7)$$

If the solvolyses were of limiting S_N1 type, and if the effects of solvation were constant, one would expect their rate constants to obey relations of the type

$$RT \log (k_1/k_2) = \Delta E_2 - \Delta E_1 \qquad (8)$$

The observed ratios are far less than would be expected on this basis; thus the ratio for phenyl and 9-phenanthryl at 40° predicted from Table I and eq 8 is 6×10^9, compared with a maximum observed value in 60% aqueous dioxane of 27. The reactions under consideration must therefore be very far from involving free carbonium ions; indeed, the same is true even for the solvolyses of arylmethyl chlorides in moist formic acid,[6] and of arylmethylmercuric perchlorates in acetic acid,[18] the most limiting reactions of this kind so far reported, the observed ratios being only 430 and 490, respectively.

It is true that the ratios might well be reduced somewhat by differential effects of solvation; an estimate of the magnitude of these can, however, be made from data for the protonation of aldehydes, ArCHO, where ArH is again an AH. As Culbertson and Pettit[19] have pointed out, the conjugate acids, $ArCHOH^+$, must approximate to the carbonium ions $ArCH_2^+$ in structure, since oxygen is so much more electronegative than carbon; any effects of solvation should be similar in both cases. The observed pK_A of a wide variety of carbonyl compounds, including such aldehydes, followed a linear relation of the type indicated in eq 8, the energy differences between them and their conjugate acids being calculated by an SCF-MO procedure;[20] however, the slope of the plot of pK_A *vs.* ΔE was about one-half that expected, implying that differential effects of solvation approximately halve the effect of changes in ΔE. On this basis one would expect the ratio of rate constants for the limiting solvolyses of benzyl and 9-anthrylmethyl tosylates to be about 8×10^4, still much greater than the values observed in even the least nucleophilic solvents. Evidently solvent participation is important in all cases, a conclusion in agreement with stereochemical studies of the acetolysis of 2-alkyl tosylates.[21]

These arguments suggest that all the reactions under consideration are of "push-pull" type[22,23] and that the nature of the transition state is determined almost entirely by the nucleophilicity of the medium. Increasing the water concentration in aqueous dioxane increases the rate by improved solvation of the leaving group; however the nucleophilicity of the medium changes little over the range of water concentrations studied here, so the structure of the transition state is little affected.

One can put this argument in another way. Solvation could influence the structure of the transition state by making the leaving group X more electronegative and the bond between it and carbon consequently more polar. The effect on this bond could be regarded as a relayed inductive effect, the unshared electrons of X being partly used to form hydrogen bonds to the solvent. Now a much more extreme effect of this kind should be observed in the quaternization of an amine, a process equivalent to formation of a dative bond by nitrogen to H^+ or R^+ and consequently involving effective transfer of a whole electron from nitrogen to H or R. In the case of aniline, one would expect this to lead to a secondary polarization of the CN bond, and this in turn to polarization of the π electrons (π-inductive effect). The available evidence suggests, however, that the resulting π polarization is not important.[24] One would therefore expect the much smaller polarization brought about by solvation of tosyl in $ArCH_2OTs$ to have a negligible effect on the relatively remote $ArCH_2O$ moiety.

Our next objective was to study the relationship between the structure of the transition state in solvolysis and the nature of the leaving group. This is an area which seems to have been almost completely

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[17] M. J. S. Dewar and C. deLlano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).

[18] B. G. van Leuwen and R. J. Ouellette, *ibid.*, 90, 7056 (1968).

[19] G. Culbertson and R. Pettit, *ibid.*, **85**, 741 (1963).

[20] M. J. S. Dewar and T. Morita, *ibid.*, 91, 802 (1969).

[21] A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965). In view of a query by a referee, it should be pointed out that there is no reason to suppose that the parameters in our SCF-MO treatment require modification in the case of ions in general, or arylmethyl cations in particular. Not only does it account well for the heats of formation of arenonium ions formed by protonation of hydrocarbons[4,17] and the ions R_2C^+OH formed by protonation of carbonyl compounds[20] (see above), but also for ions R^+ formed by ionization of neutral hydrocarbons R (the difference in energy between R and R^+ being of course equal to the ionization potential of R), including the benzyl cation, $PhCH_2^+$, itself; see M. J. S. Dewar, J. Hashmall, and C. G. Venier, *ibid.*, **90**, 1953 (1968).

[22] C. G. Swain, *ibid.*, 70, 1119 (1948); C. G. Swain and R. W. Eddy, *ibid.*, 70, 2989 (1948).

[23] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

[24] M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, **88**, 354 (1966), and papers cited there.

Table II. Rates of Solvolysis of Arylmethyl Derivatives in 79.5% Aqueous Dioxane and 80% Aqueous Ethanol

	First-order rate constant ($\times 10^5$ sec^{-1}) for solvolysis in					
	79.5% aqueous dioxane			80% aqueous ethanol		
Ar in $ArCH_2X$	OTs (50°)	Cl (79.2°)	Br (79.2°)	Cl (50°)	Br (50°)	I (50°)
Phenyl	25.2	0.153	4.24	0.22	5.04	2.88
2-Naphthyl	86.5	0.238	5.98	0.43	8.50	4.70
2-Phenanthryl	92.0	0.206	5.80	0.39	8.78	
3-Phenanthryl	183	0.442	8.02	0.69	12.6	
9-Phenanthryl	328	0.468	8.00	0.79	13.1	
1-Naphthyl	337	0.502	10.5	0.94	14.8	6.94

neglected by physical organic chemists[25] although a certain amount of work has been done on corresponding relations for SN2 reactions. For example, Lohman and Swain[26] have studied the rates of the bimolecular reactions of methoxide ion with alkyl derivatives RX and correlated them with an expression similar to that used in the well-known Swain-Scott treatment[27] of nucleophilicity; *viz.*

$$\log (k_x/k_{Br}) = \gamma L \qquad (9)$$

where k_{Br} is the rate constant for RBr, L is the "leaving group constant" for $X (= 0 \text{ for } X = Br)$, and $\gamma = 1$ for $R = CH_3$. The values of L correlated roughly with the acid strength of the corresponding acids HX; a linear relation would not be expected since the relative nucleophilicities of the ions X^- to protons and carbon acids need not be the same, and for other reasons which will be discussed presently. This treatment was quite successful and may be useful in some connections; of course empirical correlations of this kind are of limited theoretical value since they throw no light on the structure of the transition state.

We therefore decided to apply our technique to the problem by studying the rates of solvolysis of a number of arylmethyl derivatives $ArCH_2X$, where ArH is, as before, alternant hydrocarbon, and X are of a series of leaving groups. The results of such measurements for X = tosyl, Cl, Br, and I are listed in Table II, together with some relevant values from the literature. Unfortunately the rates for X = I could not be measured in the same solvent (aqueous dioxane) as the other derivatives since a side reaction interfered (see Experimental Section); the rates could be measured satisfactorily in 80% aqueous ethanol, but in this case only the benzyl and naphthylmethyl derivatives were sufficiently soluble. For comparison, the rates of solvolysis of the bromides were also measured in 80% aqueous ethanol; rates for the chlorides had been measured previously in this solvent.[6]

In aqueous dioxane, the rates are in the order OTs > Br > Cl. Thus in the benzyl series, the corresponding rates are in the ratios 1840:27.7:1.[28] The same order is observed[23,25] in the case of SN2 displacements, although the difference between tosylate and halide is less; thus the relative rates of reaction of ethyl tosylate, bromide, and chloride with ethoxide ion in ethanol are[23] 230:40:1. In aqueous ethanol, however, our solvolysis rates follow a pattern different from that observed in typical SN2 reactions, where iodides reacted more slowly.

Figure 2 shows corresponding Streitwieser plots for the two sets of reactions. The slope for the tosylates is much greater than those for the halides, implying a much greater degree of carbonium ion character in the transition state; this is in agreement with current ideas[23] based on less definite evidence. The plots for the halides are, however, surprising, implying a marked decrease in carbonium ion character of the transition state along the series Cl > Br > I. It has been generally assumed that the importance of bond breaking in the transition state should increase with ease of CX bond breaking,[29] and that the ease of CX bond breaking increases in the order Cl < Br < I. Our results show that this can be so for the reactions studied here only if breaking is counterbalanced by a still greater increase in bond forming (*i.e.*, participation by the nucleophile) along the series.

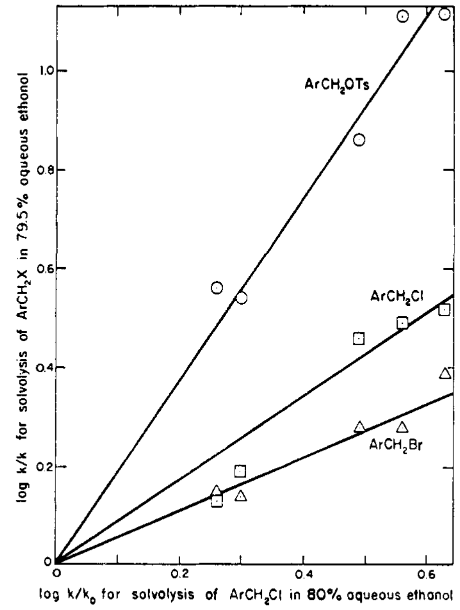

Figure 2. Streitwieser plots for the solvolysis of arylmethyl derivatives (a) in 79.5% aqueous dioxane; (b) in 80% aqueous ethanol.

The amount of nucleophilic participation presumably[23] increases with increasing departure of the central carbon atom from its initial tetrahedral geometry, the approach of the nucleophile from the side opposite the leaving group being initally hindered.

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[25] E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964.

[26] K. H. Lohman, Ph.D. Dissertation, Massachusetts Institute of Technology, 1959.

[27] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

[28] The value for benzyl tosylate is extrapolated from values measured at lower temperatures.

[29] See, *e.g.*, C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963.

The departure from tetrahedral geometry should in turn be greater, the more difficult the ionization of RX to R^+X^-. Now the energy (ΔE) required to convert RX to separated ions R^+ and X^- in the absence of a solvent is given[30] by

$$\Delta E = E_{RX} + I_R - A_X \qquad (10)$$

where E_{RX} is the RX bond energy, I_R the ionization potential of R, and A_x the electron affinity of X. Since bond energies of HX and CX bonds run roughly parallel, we would expect on this basis that the relative facility with which a series of alkyl derivatives RX (R fixed) ionize should run parallel to the strengths of the acid HX. Furthermore, this relation should carry over into solution, because the difference in energy of solvation between the ions derived from two members of the first series, R^+X^- and R^+Y^-, should be the same as the corresponding difference between H^+X^- and H^+Y^-. Since acid strength increases in the order HCl < HBr < HI, and since all these acids are at least as strong as *p*-toluenesulfonic acid, it is consequently difficult to explain our results on this basis, for the slopes of the plots indicate that ease of ionization in $ArCH_2X$ must decrease in the order OTs ≫ Cl > Br > I.

There are two factors that could account for this discrepancy. In the first place, the transition state for solvolysis of RX is a structure in which the nascent ions R^+ and X^- are still linked. There will be a coulombic interaction between them which is not taken into account in eq 10. For a given degree of bond breaking, the charges of R and X will be presumably much the same for different X; the coulombic energy will then decrease with increasing RX bond length. Since bond length increases rapidly in the order CO < CCl < CBr < CI, the corresponding decrease in coulombic energy will lead to a decrease in ease of ionization (or partial ionization) along the series.

A second factor is the increase in polarizability of atoms with increasing size, in particular in the order O < Cl < Br < I. One would expect[30] the energy required to convert the initial alkyl derivative to an SN2-like bipyramidal transition state to be less, the more polarizable the leaving group; this effect should again lead to an increased tendency to nucleophilic participation in the series O < Cl < Br < I.

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[30] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

The Solvolysis of 2-Arylethyl *p*-Toluenesulfonates[1]

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Abstract: The rates of solvolysis of a number of 2-arylethyl *p*-toluenesulfonates, $ArCH_2CH_2OSO_2C_7H_7$, where ArH is an alternant aromatic hydrocarbon, have been measured in acetic acid, formic acid, and trifluoroacetic acid, and the results interpreted in terms of various MO approximations. The reactions take place by two alternative paths, one at a rate independent of the aryl group and the other at a rate which increases with increasing conjugative power of Ar. Quantitative correlations of the rates of the latter process with appropriate MO parameters support the view that it involves a concerted process in which separation of the toluenesulfonate moiety is accompanied by rearrangement of the cation to a π complex.

In spite of extensive investigations over the last two decades, some controversy still exists concerning the intimate details of aryl participation in the solvolysis of 2-arylethyl derivatives.[4] In a recent preliminary report[3] we described some work which had a bearing on this problem; here we are presenting more complete details and additional rate studies which reinforce our earlier conclusions.

The object of this investigation was to apply a technique which has been used successfully in other connections, *e.g.*, aromatic substitution,[5] nucleophilic aliphatic substitution,[6] and the Diels–Alder reaction.[7] The idea behind this is to make use of the special properties of alternant hydrocarbons (AH)[8] by studying the relative rates of a number of reactants that differ only by a substituent derived from an AH. Since the atoms in an AH are neutral,[8] such substituents exert no field or inductive effects other than those due to the bond linking the substituent to the rest of the molecule, and the effect of this bond will of course be the same for different AH substituents. Any differences in rate must then be due to resonance interactions, and the special properties of AHs enable such interactions to be estimated with unusual facility. In the present case, the obvious way of applying this technique was to study the rates of solvolysis of 2-arylethyl derivatives $ArCH_2CH_2X$, where ArH is an alternant aromatic hydro-

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[1] This work was supported by the Air Force Office of Scientific Research through Grant Number AF-AFOSR-1050-67. A preliminary account has appeared.[3]

[2] N.A.S.A. Trainee, 1965–1968.

[3] M. D. Bentley and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **90**, 1075 (1968).

[4] (a) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) H. C. Brown, K. S. Morgan, and F. S. Chloupek, *J. Amer. Chem. Soc.*, 87, 2137 (1965); (c) D. J. Cram, *ibid.*, **88**, 3767 (1964).

[5] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[6] M. J. S. Dewar and R. J. Sampson, *ibid.*, 2789 (1956).

[7] M. J. S. Dewar and R. S. Pyron, work in course of publication.

[8] See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, for a discussion and references.