Substituent Constants for Polycyclic Aromatic Hydrocarbons. II. Solvolysis of 2-Arylethylmercuric Perchlorates in Acetic Acid[1,2]

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Abstract: The rates of solvolysis of seven 2-arylethylmercuric perchlorates at 75° in acetic acid have been determined. The logarithms of the rate constants are linearly related to the logarithms of the rates of solvolysis of the homologous arylmethylmercuric perchlorates at 25°. This correlation is consistent with the intermediacy of ethylene phenonium ions.

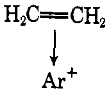
Ethylene phenonium ions as an important and discrete type of reaction intermediate are generally accepted as necessary models for the interpretation of kinetic and stereochemical data for the solvolysis of a variety of β-aryl-substituted alkyl toluenesulfonate esters.[3] The relief of steric strain in compounds such as β,β,β-triphenylethyl tosylate has been used as a point of mechanistic rebuttal which could be extrapolated to some degree to other less hindered compounds.[4]

While the stereochemical[5] and nmr[6] data for bridged phenonium ions derived from 3-phenyl-2-butyl derivatives provide almost incontestable evidence for these intermediates, the extension to the simple 2-aryl-1-ethyl compounds has given rise to controversy in this area of carbonium ion chemistry. The *p*-methoxy group of 2-arylethyl tosylate enhances the rate of solvolysis in acetic acid by a factor of 30 over that of the parent phenyl compound and in addition results in 49% rearrangement of the ^{14}C label.[7] The factor of 30 is uncorrected for both internal return and the inductive effect of the aryl group each of which should increase the value. It is only the 2-phenyl-1-ethyl systems which remain as the marginal case of the ethylene phenonium ion controversy. Their solvolysis rates have been meticulously inspected, adjusted by inductive factors, and discussed. At 75° 2-phenylethyl tosylate solvolyzes in acetic acid at a rate 2.7 times slower than ethyl tosylate.[8] However, in formic acid the phenyl compound solvolyzes 2.1 times faster than the ethyl compound. Even without the application of a negative inductive factor to adjust the observed rate, the kinetic evidence supports the postulation of the ethylene phenonium ion intermediate. Moreover, deuterium labeling[9] and ^{14}C studies[10] indicate *ca.* 10 and 5.5% rearrangement of the phenyl group in acetic acid as solvent. In formic acid the ^{14}C studies indicate that 45% of the labeled atoms have rearranged.

The solvolysis of organomercuric perchlorates indicates that the participation of the leaving group and solvent are less important in stabilizing the incipient carbonium ion than in the related reactions of tosylates.[11,12] Even in acetic acid 2-phenylethylmercuric perchlorate solvolyzes at a rate 8.3 times that of the ethylmercuric perchlorate.[13] In formic acid the rate factor is 30. Therefore, if an inductive factor of 3 is used to correct the observed rates of solvolysis, the reactions in acetic acid and formic acid proceed 95 and 99%, respectively, by an anchimerically assisted ionization route.

Substitution of other aryl groups for phenyl should give rise to solvolytic rates which are essentially completely anchimerically assisted. If this be the case, the arylethyl compounds could be compared with the arylmethyl compounds whose solvolysis rates are conceded by all to be dependent on electronic stabilization by the aromatic ring of the developing positive charge. MO calculations for the solvolysis of arylmethyl substrates using simple perturbational methods (HMO)[14] and SCF approaches[15] have been quite successful in defining the primary contribution of the stabilization of a developing delocalized cation on the observed rate. It has been pointed out that the assisted solvolysis of 2-arylethyl substrates should be amenable to the same techniques.[16] In either an intermediate spirocyclopropanoarenium ion (I) or a π complex (II) the structure of the aryl group should contribute strongly to its formation. In I the rates should correlate with the difference in π energy between Ar and the arenonium ion, whereas in II the isoconjugate structure of $ArCH_2^+$ should correlate with


I


$$\begin{array}{c} H_2C{=}CH_2 \\ \downarrow \\ Ar^+ \end{array}$$
II

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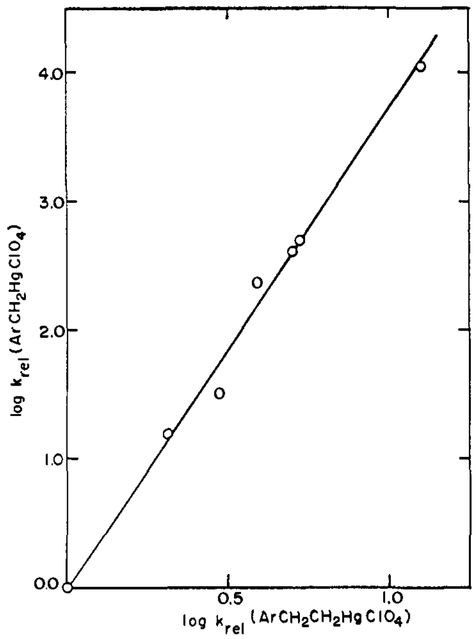

Figure 1. Correlation of the rates of solvolysis of arylmethyl and arylethyl compounds.

the difference in π energy between Ar and $ArCH_2^+$. Both of the differences in the π-bonding energy terms are linearly related. Therefore, no distinction between the two intermediates is possible from correlation lines of experimental rates and theoretical parameters. These considerations indicate that the rates of solvolysis of arylethyl substrates should parallel those of the arylmethyl substrates if only π stabilization of carbonium ion intermediates is important. If other structural contributions are important, deviations from linearity in a log k *vs.* log k plot for the two systems should result unless these contributions are self-compensating.

Results

In Table I, the rates of solvolysis of five arylethylmercuric perchlorates in acetic acid at 75.8° are recorded. The compounds include four of a 2-naphthyl-type structure and three of a 1-naphthyl-type structure.

Table I. Rates of Solvolysis of Arylethylmercuric Perchlorates at 75° in Acetic Acid

Aryl	k, sec^{-1}	Log k_{rel}
Phenyl	2.1×10^{-5}	0.0
1-Naphthyl	1.0×10^{-4}	0.70
2-Naphthyl	6.3×10^{-5}	0.47
2-Phenanthryl	4.3×10^{-5}	0.31
3-Phenanthryl	8.5×10^{-5}	0.59
9-Phenanthryl	1.1×10^{-4}	0.72
1-Anthryl	2.6×10^{-4}	1.09

Figure 1 shows a plot of log k_{rel} for arylethyl compounds *vs.* log k_{rel} for arylmethyl compounds.[1] All of the points lie reasonably close to a straight line of slope 3.8. The correlation coefficient is 0.996.

The solvolysis of 2-(1-naphthyl)ethylmercuric perchlorate yields 99% mercury and 92% 2-(1-naphthyl)ethyl acetate. The yield of mercury was determined by dissolving it in fuming nitric acid and titrating the mercuric ion of a dilute aliquot with silver ion after a known excess of thiocyanate had been added. 2-(1-Naphthyl)ethyl acetate was identified by its nmr and vpc retention time. The yield of this product was determined by integration with a planimeter of the nmr spectrum of a sample containing bibenzyl as an internal reference.

Discussion

The products of the reaction of 2-(1-naphthyl)ethylmercuric perchlorate in acetic acid are consistent with the general scheme proposed for the formation of carbonium ions from alkylmercuric ions by means of expulsion of mercury as a neutral leaving group.[11] The reaction is clearly a nucleophilic substitution and not an elimination reaction.

The linearity of the log k–log k plot given in Figure 1 indicates that the solvolysis of arylethylmercuric perchlorates are sensitive to the same electronic features of the aryl ring as are the solvolysis of the arylmethymercuric perchlorates. The slope of the correlation line combined with the ρ^+ previously given for the arylmethyl compounds (-7.0)[1,17] gives $\rho^+ = -1.8$ for the arylethyl compounds at 75°. Applying an inverse dependence correction factor for a change to 25° yields $\rho^+ = -2.1$. A linear correspondence of the arylmethyl and arylethyl solvolytic rates would not be observed if participation of the aryl group were not complete in all compounds. The linearity supports our contention (*vide supra*) that the solvolysis of 2-phenylethylmercuric perchlorate is completely anchimerically assisted.

A plot of log k *vs.* the NBMO coefficient a_{or} (proportional to ΔE_π) has been given for the solvolysis of arylethyl tosylates in both formic acid and acetic acid.[16] In the case of acetolysis the data are represented by two lines intersecting at the datum point for the 1-naphthyl compound. However, a reasonable linear correspondence between log k and a_{or} is found for the data in formic acid. The correlation coefficient is 0.985.

The extent of charge delocalization in the solvolysis of the arylethylmercuric perchlorates and the arylethyltosylates is reflected by the difference in the rates for the phenyl and the 1-naphthyl compounds. The rate factor is 5.0 and 3.95 for the mercury compounds and the tosylates, respectively. As previously reported the solvolysis of the mercury compounds is more dependent on substrate structure for stabilization of the positive charge than is the case for the tosylate solvolysis. Furthermore the data for the mercury compounds are for acetolysis whereas the tosylate data are for formolysis.

The rate factor for the solvolysis of benzylmercuric and 1-naphthylmercuric perchlorates is 400 and reflects a larger charge delocalization into the aromatic ring than is the case for the arylethyl compounds. The ethylene bridge of the phenonium ion must support a more substantial fraction of the positive charge than does the methylene group in the arylmethyl cations. The contributing resonance structures for the ethylene

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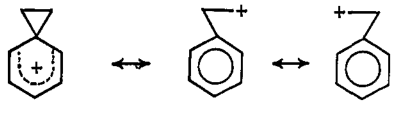
[17] R. J. Ouellette, Ph.D. Thesis, The University of California, Berkeley, 1962.

Table II. Analytical Data for Arylethylmercuric Acetates

Aryl	Calcd, % C	Calcd, % H	Calcd, % Hg	Found, % C	Found, % H	Found, % Hg	Mp, °C
Phenyl							83–84
1-Naphthyl	40.51	3.40	48.37	40.74	3.40	48.72	104–105
2-Naphthyl	40.51	3.40	48.37	40.61	3.23	48.38	117–118
2-Phenanthryl	46.50	3.46	43.14	46.58	3.42	43.10	95–97
3-Phenanthryl	46.50	3.46	43.14	46.65	3.49	43.01	106–107
9-Phenanthryl	46.50	3.46	43.14	46.62	3.61	43.26	165–166
1-Anthryl	46.50	3.46	43.14	46.60	3.59	43.22	108–109

phenonium ion qualitatively accounts for this observation.



It is interesting to note that compounds of the 1-naphthyl- and 2-naphthyl-type structures fall on the same correlation line. Steric hindrance to planarity has been suggested to account for the relatively slow solvolysis rates of 1-naphthyl-type structures.[14,18] If such hindrance is important[19,20] then there must be a compensatory steric feature which is operative in the solvolysis of the arylethyl compounds. The internuclear distance separating one of the methylene protons and the *peri*-H is approximately 1.6 Å for the planar arylmethyl cation. There are two hydrogens in the symmetrical ethylene phenonium ion whose internuclear distance from the *peri*-H is 1.9 Å. Therefore, there is qualitative support for a compensatory steric factor which could be operative in the solvolysis of arylethylmercuric perchlorates of the 1-naphthyl-type structure.

Experimental Section

Arylethylmercuric Acetates. The known 2-arylethanols[20-25] were converted either into the 2-aryl-1-bromoethanes[21,26,27] by phosphorus tribromide or into the 2-aryl-1-chloroethanes[25] by thionyl chloride. The corresponding 2-arylethylmercuric halides were prepared by the Grignard method. Each Grignard solution was filtered through a dry glass wool plug under a nitrogen atmosphere prior to its reaction with the mercuric halide in ether solution. The alkylmercuric halides were converted into the alkylmercuric acetates by reaction with silver acetate in anhydrous methanol. The melting points and elemental analysis of the 2-arylethylmercuric acetates are given in Table II. Each compound was recrystallized from either hexane or heptane.

Kinetic Analysis. The reactions were carried out at 75.8° at concentrations of approximately 0.02 *M* for both the organomercuric acetate and perchloric acid. Acetic anhydride was added to distilled acetic acid to produce a 0.26 *M* solution. Aliquots of the solution (2 ml) were sealed in test tubes and immersed in a constant-temperature bath maintained at 75.8°. At appropriate time intervals the test tubes were removed and frozen in a Dry Ice–acetone bath. After allowing the tubes to warm to room temperature the contents were removed and transferred into a flask. The titer of the solution was determined by adding a known excess of thiocyanate and back-titrating with silver ion using ferric ion as the indicator.[28]

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