A Kinetic Dissection of Simultaneous Ar$_1$-5 Aryl Participation and Unassisted Solvolysis[1]

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Abstract: Four 4-aryl-1-butylmercuric perchlorates, in which the aryl groups are *p*-chlorophenyl, phenyl, *p*-tolyl, and *p*-anisyl, respectively, have been solvolyzed in acetic acid at five temperatures covering the range of 62.5–112.5°. The Arrhenius and Hammett correlations of the observed rate data are suggestive of the operation of two simultaneous rate processes. Using the Hammett relationship as a guide the observed rate constants are dissected by a computer program to yield assisted and unassisted rate constants. The activation parameters for the two pathways and the Hammett correlation for the assisted pathway are associated with high correlation coefficients and provide strong evidence for the proposed simultaneous rate processes.

It has been proposed over a period of 20 years that solvolytic reactions of primary and secondary arenesulfonates with neighboring aryl groups occur with aryl group bridging in the ionization step.[3,4] Analysis of the reactions of such compounds suggests that there are two competing pathways each with its own specific rate constants designated k_Δ and k_s where the k_Δ refers to the aryl assisted rate and the k_s the unassisted rate where solvent is presumably involved in the displacement of the leaving group. Brown and coworkers have suggested that there are inconsistencies in the theory and its application.[5]

Major emphasis has been placed on 2-phenylethyl, 3-phenyl-2-butyl, 1-phenyl-2-propyl compounds for which both product studies and kinetic analysis are still in progress.[6] By contrast compounds which can react *via* an Ar$_1$-5 phenyl participation mechanism have been little studied from a kinetic point of view since the initial work of Winstein.[7] 4-Aryl-1-butyl derivatives should be free from many of the secondary rate effects created by the introduction of an aryl group as observed in the 2-arylethyl and related derivatives. Steric effects and any related conformational changes due to the phenyl ring should be minimal. Furthermore, semiempirical corrections of the observed rate for polar effects should not be of sufficient magnitude to diminish the expected rate enhancements due to aryl participation.

The rate enhancements observed by Winstein[7] are reasonably small; the *p*-methoxy group increases the observed rate by only 31% for the 4-aryl-1-butylbenzene sulfonates in acetic acid. Each rate constant was dissected into k_Δ, the rate of anchimerically assisted solvolysis and k_s, the rate of the unassisted process. Product compositions are related to k_Δ and k_s assuming that these constants are associated with formation of a tetralin and an ester.

Recent studies in the 2-arylethyl, 3-aryl-2-butyl, and 1-aryl-2-propyl systems have illustrated the utility of Hammett correlations and associated curvature as a tool for the dissection of observed rate constants into component rate constants.[6] Product studies are an integral part of the analytical method. With the general acceptance of this approach at this time it now appears appropriate to resubmit our observation on the 4-aryl-1-butylmercuric perchlorate solvolysis in acetic acid.[8]

The rates of solvolysis of organomercury salts are markedly sensitive to structural changes.[9] With the anticipated large differences in the rates of the reaction the 4-aryl-1-butylmercuric perchlorates should provide an adequate system for the complete kinetic dissection of assisted and unassisted processes independent of any assumption regarding the mode of formation of product.

Results and Discussion

The observed rate constants for the solvolysis of the four 4-aryl-1-butylmercuric perchlorates in acetic acid at five temperatures are given in Table I. Each reported rate constant is the average value of triplicate runs. The individual runs have correlation coefficients greater than 0.995 over two half-lives. Agreement between individual runs is within 2% of the reported average and many runs agree within 1%.

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[8] Our original paper of 6 years ago was objected to so strenuously by one referee that we withdrew the manuscript. At that time only hand calculations were available and the referee suggested that the observed curvature of the Hammett plots were not real and that straight line representations were entirely adequate. Braced by both computer calculations and the company of related approaches[6] on similar systems we now find our approach to be more acceptable.

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Table I. Rates of Solvolysis of 4-Aryl-1-butylmercuric Perchlorates in Acetic Acid[a]

Aryl	T, °K					$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	r
	385.65	373.15	360.65	348.15	335.65			
p-Anisyl	521	138	33.7	7.73	1.64	28.93	0.90	0.9999
p-Tolyl	274	65.5	14.3	3.00	0.564	31.10	5.26	0.9999
Phenyl	219	48.7	9.75	1.88	0.320	32.85	9.38	0.9999
p-Chlorophenyl	202	44.0	8.37	1.56	0.255	33.63	10.80	0.9999

[a] $\times 10^6$ sec^{-1}. [b] kcal/mol. [c] Cal/deg.

The activation parameters and correlation coefficients given in Table I are calculated by a least-squares computer program using the double precision mode.

While the correlation coefficients are very high they are lower than would be expected from the accuracy of the rate constants, the magnitude of the rate differences, and the range of temperatures employed. While the Arrhenius-type plots shown in Figure 1 are drawn to be linear, a close examination of the data suggests that the data exhibit curvature with the apparent enthalpy of activation increasing with increasing temperature. However, clearly one cannot use the Arrhenius treatment of the data as the sole basis for suggesting the possibility of competing rate process.

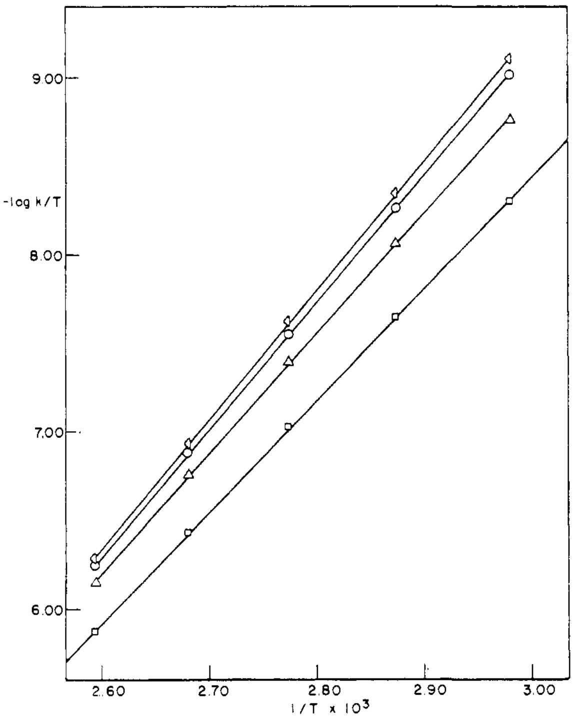

Figure 1. Log k/T for 4-aryl-1-butylmercuric perchlorates *vs.* $1/T$: □, 4-(*p*-anisyl)-1-butylmercuric perchlorate; △, 4-(*p*-tolyl)-1-butylmercuric perchlorate; ○, 4-phenyl-1-butylmercuric perchlorate; ▷, 4-(*p*-chlorophenyl)-1-butylmercuric perchlorate.

More dramatically, in Figure 2, plots of the observed rate constants *vs.* σ^+ as a function of temperature clearly indicate nonlinear relationships. The linearity of the Hammett plots improves at the lower temperatures. In Table II the ρ^+ values for an assumed linear Hammett relationship and the corresponding correlation coefficients as calculated by a least-squares computer program with double precision are listed. Clearly the magnitude of the change of ρ^+ with temperature is excessively large. Since ρ^+ is usually approximately inversely proportional to the absolute temperature, a change of 15% would be expected over the temperature range utilized, rather than the 100% change observed. The excessively large change in ρ^+ is suggestive that two rate processes are occurring whose enthalpies of activation are markedly different. Furthermore, the smooth ordering of correlation coefficients for the assumed linear Hammett correlation with temperature indicates that a single rate process cannot be used to describe the solvolysis reaction.

Table II. Hammett Parameters

T, °K	Observed rates		Assisted rates	
	ρ^+	r	ρ^+	r
385.65	−0.4612	0.9869	−1.040	0.9992
373.15	−0.5565	0.9910	−1.070	0.9997
360.65	−0.6759	0.9952	−1.103	0.9999
348.15	−0.7766	0.9974	−1.138	1.000
335.65	−0.9026	0.9984	−1.183	0.9999

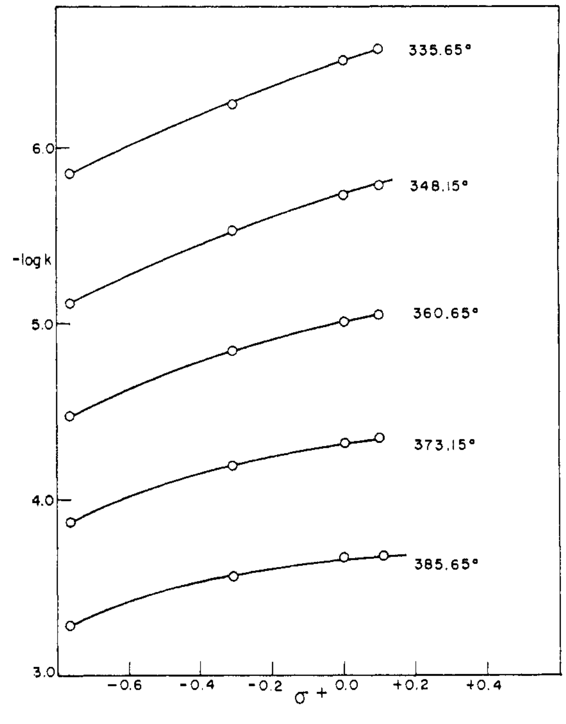

Figure 2. Log k of total solvolysis rates *vs.* σ^+.

Two simultaneous first-order processes are not detectable by rate studies at a single temperature. The detection of two processes by examination of an Arrhenius plot would be feasible only if the activation parameters for the two processes are very different, thus leading to distinct curvature. However, a Ham-

Table III. Rates of Unassisted Solvolysis in Acetic Acid[a]

	T, °K							
	385.65	373.15	360.65	348.15	335.65	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	r
4-Arylbutyl-	166	34.0	6.00	1.00	0.130	35.69	16.84	0.9999
Butyl-	190	41.8	7.62	1.20	0.172	35.46	16.56	1.000

[a] $\times 10^6$ sec^{-1}. [b] Kcal/mol. [c] Cal/deg.

Table IV. Rates of Assisted Solvolysis of 4-Aryl-1-butylmercuric Perchlorates in Acetic Acid[a]

	T, °K							
Aryl	385.65	373.15	360.65	348.15	335.65	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	r
p-Anisyl	355	104	27.7	6.73	1.51	27.41	−3.76	1.000
p-Tolyl	108	31.5	8.30	2.00	0.432	27.70	−5.35	1.000
Phenyl	53.0	14.7	3.75	0.875	0.190	28.49	−4.71	1.000
p-Chlorophenyl	36.0	10.0	2.37	0.560	0.125	28.96	−3.93	0.9999

[a] $\times 10^6$ sec^{-1}. [b] Kcal/mol. [c] Cal/deg.

mett plot will exhibit nonlinearity if one of the processes is substituent independent, of differing substituent sensitivity, or of opposite sign than for the second process. The linearity of the Hammett plot will vary with temperature if the fraction of the substrate proceeding by the two paths varies; that is, if the activation parameters differ. The apparent response to substituents as a function of temperature would then be expected to be substantially different from that predicted from an inverse relationship.

In order to (1) increase the correlation coefficients of the Arrhenius plots, (2) increase the correlation coefficients of the Hammett plots, and (3) reduce the change of ρ^+ with temperature, an arbitrary dissection of the total rate into two separate contributing first-order processes was attempted. The procedure involves an iterative process to minimize all errors associated with the Hammett and Arrhenius expressions. A computer program was designed such that arbitrary rate constants for the rate of the unassisted solvolysis were subtracted from the rate constants of each compound at a given temperature in order to increase the linearity of the Hammett plot as evidenced by the correlation coefficients. Values larger than those ultimately chosen for the unassisted solvolysis change the curvature in the opposite sense and decrease the correlation coefficients. This process was carried out at all temperatures and the fractional correction is largest at the highest temperature. In order to restrict further the choice of the arbitrary rate constants for the unassisted process, it was necessary to obtain a reasonable Arrhenius plot for the unassisted rate constants. In addition all of the assisted rate constants for each compound had to yield satisfactory Arrhenius plots.

The best values for the unassisted process are given in Table III with the calculated activation parameters and correlation coefficient. The difference between the total rates and the unassisted rates yields the assisted rates which are tabulated in Table IV with the activation parameters and correlation coefficients. The fit of the Arrhenius plots for the assisted rates which are shown in Figure 3 are slightly better than those in Figure 1. The principal observable change is that of conversion of a family of convergent lines to that of a family of parallel lines. The correlation coefficients more clearly show the improvement in the fit. More strikingly the Hammett σ^+ plots in Figure 4 are linear with ρ^+ values as given in Table II which are inversely proportional to temperature.

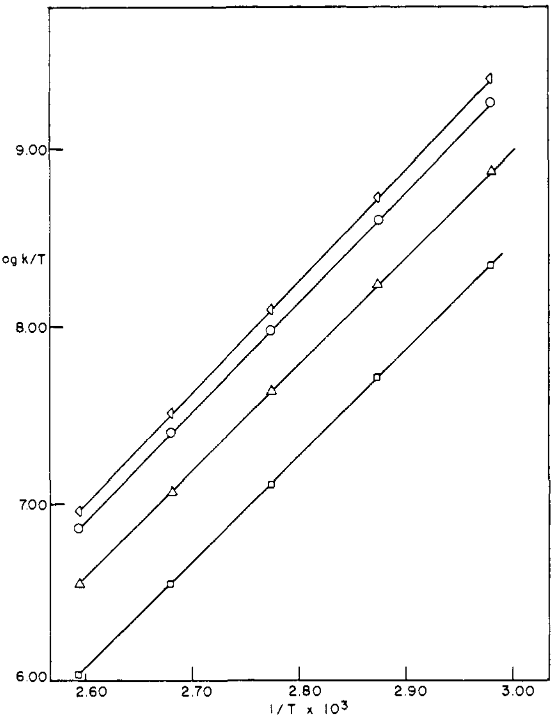

Figure 3. Log k/T for 4-aryl-1-butylmercuric perchlorates *vs.* $1/T$ for assisted rates: □, 4-(p-anisyl)-1-butylmercuric perchlorate; △, 4-(p-tolyl)-1-butylmercuric perchlorate; ○, 4-phenyl-1-butylmercuric perchlorate; ▷, 4-(p-chlorophenyl)-1-butylmercuric perchlorate.

The ratio of ρ^+ values at 335.65 and 385.65°K is 1.14 whereas the inverse of the ratio of the temperatures is 1.15. This excellent internal consistency lends considerable support to the existence of an assisted solvolytic pathway. Additional support of the model is provided by the fact that the correlation coefficients for the Hammett plots (Figure 4) as listed in Table II are essentially independent of temperature.

It was anticipated that the estimated rates for the unassisted process would be close to that of 1-butylmercuric perchlorate but an exact equality need not exist. The rate constants, activation parameters, and

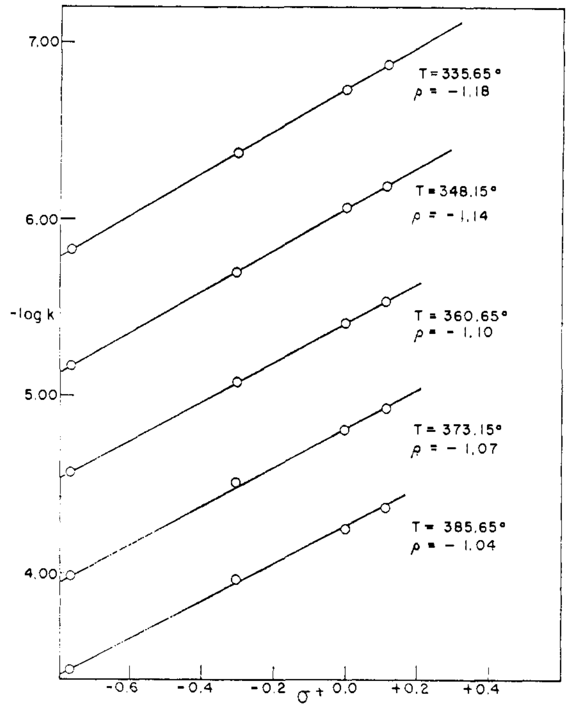

Figure 4. Log k of assisted rates *vs.* σ^+.

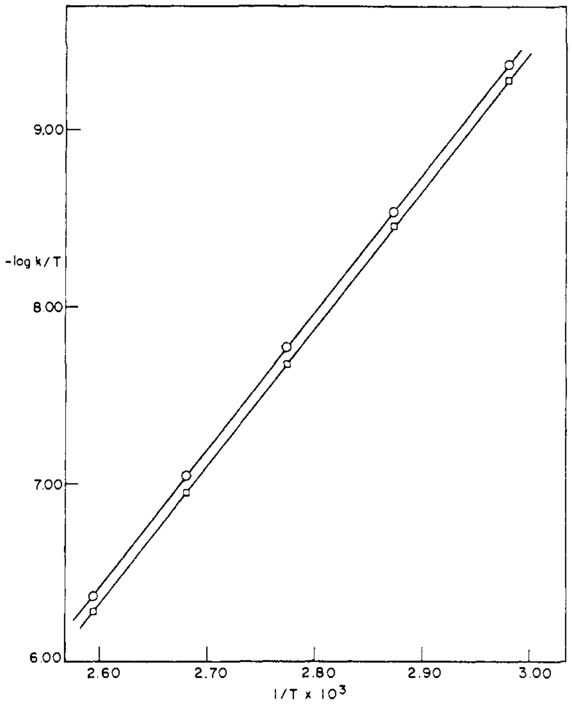

Figure 5. Log k/T for unassisted solvolysis: □, 1-butylmercuric perchlorate; ○, 4-aryl-1-butylmercuric perchlorate.

correlation coefficients for 1-butylmercuric perchlorate are tabulated in Table III and the Arrhenius plot compared in Figure 5 with that of the estimated unassisted rate for the 4-aryl-1-butylmercuric perchlorates. The rates for the unassisted solvolysis are approximately 20% lower than that of the butyl system. This small difference is most reasonably attributed to a polar effect of the aryl group which is electron withdrawing. A σ^* value for $C_6H_5(CH_2)_3-$ may be estimated as +0.03 from the σ^* value of $C_6H_5(CH_2)_2-$[10] using a fall-off factor of 2.8 per CH_2 unit. Since the difference in σ^* between *n*-propyl and 3-phenylpropyl is approximately 0.15 and gives rise to only a 20% rate difference the differences in unassisted rates for the 4-aryl-1-butylmercuric perchlorates must be very small. All the σ^* values for the 3-arylpropyl groups involved in this study can be estimated to lie in the range of +0.02 to +0.04.[11,12] Therefore the differences in the unassisted rates for the 4-(*p*-chlorophenyl)-1-butylmercuric perchlorate and the 4-(*p*-anisyl)-1-butylmercuric perchlorate can only be in the order of 2% of the value chosen. This small difference justified the use of single values of unassisted rates independent of the type of aryl group. Secondary effects would be expected to be beyond detection and their introduction would not increase the fit of the data.

The activation parameters for the assisted rates are dramatically different from those of the unassisted process. There is a lowering of the enthalpy of activation and a negative change in the entropy of activation for the assisted process as compared to the unassisted process. The interplay for the two processes and the resultant change in the Hammett and Arrhenius plots is evident in Figures 1–4. In the solvolysis of benzenesulfonate esters differing $\Delta S^\ddagger$ values have been taken as characteristic of the individualistic character of the unassisted and assisted reaction pathways.[3,4] However the $\Delta S^\ddagger$ for the unassisted reaction is more negative than for the aryl assisted reaction—an ordering which is exactly opposed to that observed in this study. Since the reason for the ordering of $\Delta S^\ddagger$ for benzenesulfonate solvolysis is not known unambiguously there is little reason to be concerned about an opposite order. In benzenesulfonate solvolysis reactions the unassisted process is purported to possess S_N2 character and ordering of solvent in the transition state is involved. In contrast to benzenesulfonate solvolysis the mercury compounds involve a neutral leaving group. Furthermore, the reaction possesses more S_N1 character and is less sensitive to the nucleophilicity of the solvent. There is also evidence that solvent may be coordinated with mercury in the ground state and probably is substantially released in the transition state.[9]

A comparison of the ρ^+ values for various related carbonium ion reactions in which positive charge is delocalized into an aromatic ring reveals an interesting relationship not previously discussed by other workers. In Table V are given the ρ^+ values for the rates of

Table V. Comparative σ^+ Values

Substrate	Leaving group: Hg	Leaving group: OTs
Benzyl	−7.0	−5.7
2-Arylethyl	−2.9	−2.5
4-Arylethyl	−1.2	−0.9

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(12) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956.

Table VI

Compound	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
4-(*p*-Anisyl)-1-butylmercuric bromide	141–142	29.77	3.41	29.68	3.38
4-(*p*-Tolyl)-1-butylmercuric bromide	129–130	30.89	3.53	30.91	3.54
4-Phenyl-1-butylmercuric bromide	124–125	29.03	3.17	28.95	3.20
4-(*p*-Chlorophenyl)-1-butylmercuric bromide	84–85	26.80	2.70	26.89	2.65
4-(*p*-Anisyl)-1-butylmercuric acetate	76–77	37.10	4.31	37.23	4.31
4-(*p*-Tolyl)-1-butylmercuric acetate	65–66	38.56	4.48	38.44	4.54
4-(Phenyl-1-butylmercuric acetate	50–51	36.68	4.11	36.88	4.23
4-(*p*-Chlorophenyl)-1-butylmercuric acetate	85–86	33.73	3.54	33.79	3.49

benzyl and the assisted rates of 2-phenylethyl and of 4-phenylbutyl where the leaving groups are mercury and a sulfonate anion. The data for the acetolysis of the benzyl tosylates have only recently been made available.[13] When compared to the acetolysis of the benzylmercuric perchlorates[14] it is clear that the mercury compounds are more sensitive to substituent effects than are the tosylates as has been noted previously by Jensen.[9] The 2-arylethyl compounds stand in the same order as for the benzyl compounds. However it should be noted that while the k_Δ for the acetolysis of the tosylates has been determined, the k_Δ for the mercury compounds has not. Using the observed rate constants for the arylethylmercuric perchlorates the approximate ρ^+ can be calculated because it is clear from the observed rate accelerations that k_s is small with respect to k_Δ. Therefore the calculated ρ^+ represents a minimum absolute value. In order to obtain the ρ^+ for the acetolysis of the 4-arylbutyl tosylates the authors have used the media value of the rate acceleration factor range for methoxyl over hydrogen estimated by Winstein.[7] This estimated ρ^+ stands in the same order to the other compounds as that exhibited by the mercury compounds reported in this paper.

Electrophilic aromatic substitution reactions by alkyl groups might be considered as reference reactions from which estimates of ρ^+ values for phenyl-assisted solvolysis could be derived. Data are available for ethylation using ethyl bromide and gallium bromide in ethylene chloride at 25°.[15] However, the conditions of the reaction are clearly different than those of the acetolysis reaction and, therefore, the $\rho^+ = -2.4$ is of little significance in an absolute sense. Furthermore it has been amply demonstrated for bromination, mercuration, and desilylation that the selectivity of the electrophilic species is a function of its source.[15]

Both the 2-arylethyl- and 4-arylbutylphenonium ion derivatives appear to have less charge delocalized into the aromatic ring than the benzyl cations. One possible rationale for this is that the transition state does not involve a fully developed symmetrical phenonium ion. The ordering of ρ^+ is consistent with this hypothesis as one would expect the transition state of the 2-arylethyl derivatives to lie further along the reaction coordinate as necessitated by the formation of the strained three-membered ring. In the case of the 4-arylbutyl derivatives the transition state is achieved earlier and less charge is delocalized into the aromatic ring. However, if symmetrical phenonium ions are formed in the transition state then the difference in the charge developed in the aromatic ring indicates that the differential charge is located in the spiro bridge. Consequently one would have to accept that the charge is more stable on the two external methylene carbons of a tetramethylene fragment than the two methylene carbons of a dimethylene unit. While this result is an intuitively acceptable consequence of the contributing resonance forms representing the phenonium ion, there appears to be no unambiguous way to distinguish between the two possibilities suggested without significantly altering the substrate structure.

Experimental Section

Kinetic Method. Solutions of 4-aryl-1-butylmercuric perchlorates in anhydrous acetic acid which was 0.08 *N* in acetic anhydride were prepared by adding the proper amount of the 4-aryl-1-butylmercuric acetate to the acetic acid solution which was approximately 0.0225 *N* perchloric acid. Aliquots of 2 ml were placed in Pyrex test tubes and sealed. The tubes were immersed in a constant-temperature bath maintained at the desired temperature. The fluctuation in temperature was approximately 0.02°. Samples were periodically withdrawn and frozen in an acetone–Dry Ice mixture. At the conclusion of the run, the tubes were opened and the contents were transferred to a flask containing sodium thiocyanate solution. Titration of excess thiocyanate determined the concentration of mercuric salt present in the sample.[9a,16]

Preparation of 4-Aryl-1-butylmercuric Bromides. The Grignard reagent was prepared from the proper alkyl bromide and the concentration determined by the base produced by quenching an aliquot of the solution. Addition of a solution of the Grignard reagent to mercuric bromide in ether yielded the alkylmercuric bromide in yields of approximately 80% after recrystallization from absolute ethanol. The melting points and analysis of each compound are recorded in Table VI.

Preparation of 4-Aryl-1-butylmercuric Acetates. Equimolar amounts of alkylmercuric bromide and silver acetate were stirred in absolute methanol for 16 hr. The system was shielded from light. Silver bromide was removed by filtration. Evaporation of the methanol by rotary evaporator yielded crystalline compounds in nearly quantitative yields. Recrystallization was accomplished using hexane. The melting point and analysis of each compound are recorded in Table VI.

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