benzhydryl chloride,[49] *p*-chlorobenzhydryl chloride,[49] benzhydryl chloride (Aldrich), *p*-methylbenzhydryl chloride,[49] and *p,p'*-dimethylbenzhydryl chloride.[50]

(49) K. E. Hamlin, A. W. Weston, F. E. Fishcer, and R. J. Michaels, Jr., *J. Amer. Chem. Soc.*, **71**, 2731 (1949).
(50) J. F. Norris and J. T. Blake, *J. Amer. Chem. Soc.*, **50**, 1808 (1928).

Solvents. Ethanol was distilled from magnesium ethoxide and mixed (v/v) with double-distilled water.

Kinetic Procedure. Rates were determined conductimetrically as previously described.[5]

Product Determination. Product ratios were determined by direct gas chromatographic analysis of reaction mixtures. A 6 ft × 1/8 in. column packed with 5% SF96 on 60–70 mesh Anakrom ABS was used.

Ion-Pair Identification by Means of a Stability–Selectivity Relationship[1]

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Abstract: Rates and products for the aqueous ethanolysis of 2-adamantyl arenesulfonates are reported and these data used to construct a stability–selectivity plot. A selectivity dependence on leaving group identity is observed as expected for product formation by attack on an ion-pair intermediate. Surprisingly water is found to be more nucleophilic than ethanol for attack on these intermediates and it is concluded that the intermediates can only be solvent-separated ion pairs. Additionally, the aqueous ethanolyses of a series of benzhydryl benzoates are studied. For these derivatives a constant selectivity is observed despite changes in leaving group. Although such a result would seem to implicate product formation only from free carbocation, we conclude that this is not the case; solvent-separated ion pairs also appear to be involved.

According to Hughes and Ingold's original formulation of the SN1 and SN2 mechanisms for nucleophilic substitution on saturated carbon, reaction *via* the SN1 pathway (eq 1), but not the SN2 pathway (eq 2), should result in product independence of leaving group X.[3] Recent research has shown ion pairs to be involved in the substitution process such that a unimolecular process may also yield II or III in addition to the free carbocation IV (Scheme I).[4-6] Therefore reaction by

Scheme I

$$R{-}X \longrightarrow R^+ + X^- \xrightarrow{Nuc} R{-}Nuc^+ \quad (1)$$

$$R{-}X + Nuc \longrightarrow R{-}Nuc^+ + X^- \quad (2)$$

$$\underset{\text{I}}{R{-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{II}}{R^+X^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{III}}{R^+ \parallel X^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\text{IV}}{R^+ + X^-}$$

$$k_s^{\text{I}}[Nuc] \quad k_s^{\text{II}}[Nuc] \quad k_s^{\text{III}}[Nuc] \quad k_s^{\text{IV}}[Nuc]$$

$$R{-}Nuc^+ \quad R{-}Nuc^+ \quad R{-}Nuc^+ \quad R{-}Nuc^+$$

an SN1 mechanism (k_1, k_2, or k_3 rate limiting) can also show a product dependence on leaving group if tight ion pair (II) or solvent-separated ion pair (III) is formed in the rate-limiting step and rapidly destroyed by nucleophilic attack or elimination. If the rate-limiting step of a substitution reaction can be demonstrated to be unimolecular, a dependence of products on leaving group provides evidence for involvement of ion pairs II or III in the product-determining step. Cocivera and Winstein[7] have applied this concept to explain their observation of changes in the percentage of isobutylene formed from the solvolysis of *tert*-butyl derivatives. Furthermore, if our previous interpretation[8] of stability–selectivity relationships in solvolytic substitution relations is correct, this product dependence on leaving group should be very definite one, varying according to the extent of dissociation when attack occurs and according to stability of the solvent-separated ion pair if it is involved; this relationship can be expressed in terms of the observed selectivity and the selectivity for attack by ethanol and water (or any other pair of nucleophiles) on intermediates *i*, eq 3–6, where

$$S_i = (\log k_E/k_W)_i \quad (3)$$

$$S_{obsd} = \sum_i a_i S_i \quad (4)$$

$$S_i = k_i \qquad i = \text{I, II, and IV} \quad (5)$$

$$S_{III} \propto \text{stability of III} \quad (6)$$

a_i represents the fraction of products from attack on *i*, and k_i is a constant for I, II, and IV but not for III.

The purpose of this article is to examine the possibility that stability–selectivity relationships may exist

(1) A preliminary account of portions of this work has appeared in communication form: J. M. Harris, J. F. Fagan, F. A. Walden, and D. C. Clark, *Tetrahedron Lett.*, 3023 (1972).
(2) Address correspondence to this author at the Department of Chemistry, University of Alabama–Huntsville, Huntsville, Ala. 35807.
(3) C. K. Ingold, "Structures and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, New York, N. Y., 1969.
(4) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965).
(5) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions," Vol. 2, M. Szwarc, Ed., Wiley, New York, N. Y., in press.
(6) J. M. Harris, *Progr. Phys. Org. Chem.*, **11**, 89 (1974).
(7) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).
(8) J. M. Harris, D. C. Clark, A. Becker, and J. F. Fagan, *J. Amer. Chem. Soc.*, **96**, 4478 (1974).

for limiting (without kinetically significant nucleophilic solvent assistance) solvolytic substitution reactions in which only the leaving group is changed, and also to determine the usefulness of any such relationships for identification of ion-pair types in the aqueous ethanolysis of 2-adamantyl arenesulfonates and benzhydryl benzoates.

Results and Discussion

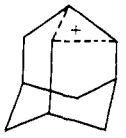
2-Adamantyl Arenesulfonates. The 2-adamantyl derivatives were chosen for study because of their convenient rates of reaction, lack of elimination or rearrangement, and ready synthesis and because of the large amount of previous work on their solvolysis mechanism. Schleyer and his coworkers have conducted an extensive study of the 2-adamantyl system, utilizing several different probes of solvolysis mechanism, and have concluded that this substrate is one of the very few secondary substrates known to solvolyze by a limiting mechanism.[9-12] A limiting solvolysis can have any of three steps on Scheme I (k_1, k_2, or k_3) as rate limiting. On the basis of Shiner's theory of α-deuterium isotope effects[13] and the observation of maximum effects for 2-adamantyl solvolysis,[10,14] this rate-limiting step is indicated to be k_2—interconversion of tight and solvent-separated ion pairs. Support for this interpretation can be drawn from Bone and Whiting's[15] observations of excess retained solvolysis product upon reaction of 2-adamantyl derivatives. As has been noted,[1,5,6,16] solvolysis to give products almost, but not completely, racemized is indicative of competitive backside nucleophilic attack on a solvent-separated ion pair (pathway a, **1**) and frontside "collapse" (pathway b, **1**) of a solvent-separated ion pair.

$$\text{SOH} \xrightarrow{a} \text{R}^+ \xleftarrow{b} \text{SOH X}^-$$

1

Whiting and his coworkers[17] have also observed a small amount of rearrangement (0.4%) upon acetolysis of 2-adamantyl tosylate. This result is interpreted by Whiting as demonstrating neighboring carbon participation in 2-adamantyl solvolysis. We view such participation as highly unlikely in view of the high α-deuterium isotope effect observed for this substrate[10,14,18] and in view of the unsymmetrical nature of such a nonclassical cation, **2**.

The evidence seems most consistent with solvolysis of 2-adamantyl derivatives by rate-limiting formation of a solvent-separated ion pair (III) from a tight ion pair (II)



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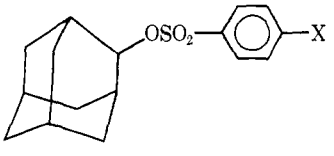
followed by rapid destruction of III. Most secondary substrates react by one or both of the following pathways: (1) nucleophilic attack on neutral substrate (I) or tight ion pair (II); or (2) neighboring group attack on I or II to give a nonclassical ion followed by dissociation to III or IV and subsequent nucleophilic destruction;[4-6] nonclassical ions cannot be attacked at the tight ion pair stage because the backside is "protected." The 2-adamantyl system is novel in that the backside of the reaction center is sterically shielded from nucleophilic attack and there are no carbon–carbon bonds or carbon–hydrogen bonds stereoelectronically capable of giving neighboring group participation. Thus the substrate is "forced" to dissociate to the solvent-separated ion pair stage before it can react with solvent nucleophile. Further dissociation to the free cation stage would be highly unlikely for an unstabilized, secondary, solvent-separated ion pair. If k_2 is the rate-determining step, internal return (k_1) is probably important. However, the 2-adamantyl solvent-separated ion pair is probably not stable enough to give significant amounts of external ion-pair return (k_{-2}), but will probably undergo rapid nucleophilic attack.[4-6] Consistent with this interpretation, k_{-2} is indicated not to occur for the more stable *exo*-2-norbornyl system.

We have determined the rates and products from aqueous ethanolysis of a series of five 2-adamantyl arenesulfonates, **3** (Table I). Product selectivities for



3, X = OCH_3, CH_3, H, Br, and NO_2

Table I. Rates and Products for 2-Adamantyl *p*-X-Benzenesulfonates in 70% (v/v) Ethanol

X	Temp, °C	$k \times 10^4$ sec^{-1} [a]	ROH/ROEt[b]	Log k_E/k_W
OCH_3	100.2	5.79 ± 0.19	1.94	−0.15
	75.8	0.472 ± 0.010		
	75[c]	0.433		
CH_3	100.3	7.94 ± 0.01	2.56	−0.27
	75.8	0.621 ± 0.010		
	75[c]	0.570		
H	100.4	13.5 ± 0.1	3.25	−0.37
	75.8	1.07 ± 0.01		
	75[c]	0.985		
Br	100.6	36.6 ± 0.3	3.05	−0.34
	75.8	3.39 ± 0.01		
	75[c]	3.13		
NO_2	76.2	23.6 ± 0.3	5.20	−0.58
	50.2	1.17 ± 0.02		
	75[c]	20.4		

[a] Determined conductimetrically. [b] Determined by vpc and accurate within 5%. Solvolysis was performed at 100° for approximately 10 half-lives, and all products are shown to be stable to the reaction conditions. Substrate concentrations were 0.01 *M*. [c] Calculated.

(9) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).
(10) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 2551 (1971).
(11) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971).
(12) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 993 (1972).
(13) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, Chapter 2.
(14) V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971).
(15) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).
(16) R. A. Sneen, *Accounts Chem. Res.*, **6**, 46 (1973).
(17) M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969).
(18) (a) D. E. Sunko and S. Borcic in ref 13, Chapter 3; (b) D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 2138 (1974).

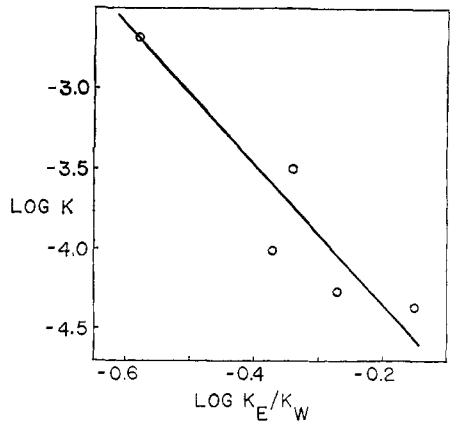


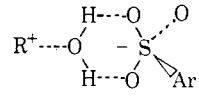
Figure 1. A stability–selectivity plot for 2-adamantyl arenesulfonate solvolysis.

ethanol and water substitution, log k_E/k_W, are determined from ether–alcohol ratios by use of eq 7.

$$k_E[EtOH]/k_W[H_2O] = ROEt/ROH \quad (7)$$

The observed product ratios do show a dependence on leaving group; as noted above, such a dependence is consistent with product formation by nucleophilic attack on an ion pair. Additionally, a plot of stability (as measured by log $k_{solvolysis}$)[8] against selectivity (Figure 1) results in a rough linear relationship with a negative slope. The negative slope (*i.e.*, water appearing to be more nucleophilic than ethanol) is noteworthy since the other substrates we have examined give a positive slope.[8] Also, other workers have shown ethanol to be more nucleophilic than water for attack on methyl halides.[12]

We concluded above that 2-adamantyl derivatives probably lead to solvolysis products by nucleophilic attack at the stage of solvent-separated ion pair. Examination of the structure of cation–arenesulfonate, solvent-separated ion pairs, **4** and **5**, shows that the ion



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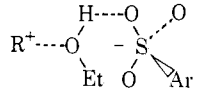

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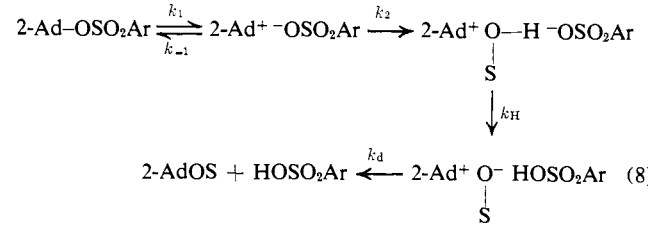
pair with water as the insulating molecule, **4**, has an additional hydrogen bond and thus should be more stable than ion pair **5**. Therefore, as the anionic portion of the ion pair becomes more stable, and the ion-pair unit becomes more stable, species **4** should become increasingly favored over **5** with the result that an increasing ROH/ROEt ratio should be produced.

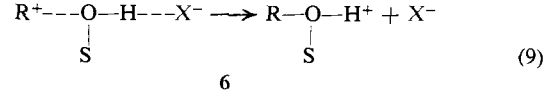
An alternative explanation for the negative slope of Figure 1 can be based on Ritchie's observation of general base catalysis for solvent attack on a presumably free triarylmethyl cation.[19] If proton transfer is the slow step in destruction of the 2-adamantyl arenesulfonate, solvent-separated ion pairs, eq 8, then the relative basicities of the leaving groups would be the controlling factor in product formation. The better leaving groups are the poorer bases. The poorer bases might be expected to be more selective and thus to increasingly favor proton removal from water which has two protons and is more acidic than ethanol; such a

(19) C. D. Ritchie, *J. Amer. Chem. Soc.*, **94**, 3275 (1972).



trend would produce an increase in ROH/ROEt with an increase in solvolysis rate. However, we question whether k_H will be slower than k_2 for the 2-adamantyl derivatives. In view of the low reactivity of 2-adamantyl derivatives, we are of the opinion that k_2 will be the slow step and that these reactions will not exhibit general base catalysis. We could detect no evidence for general base catalysis in the solvolysis of more reactive benzhydryl benzoates (below).

Collapse of solvent-separated ion pairs (*i.e.*, formation of a covalent bond between the insulating solvent molecule and the cation) should lead to a product of retained configuration, eq 9. Solvent-separated ion



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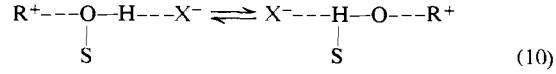
pairs can also lead to inverted product by backside attack or by isomerization of the ion pair, eq 10, fol-



(10)

lowed by collapse as in eq 9. As has been pointed out by us and by others, this retention pathway *via* solvent-separated ion pair, eq 9, offers an alternative to postulation of nonclassical ion formation to explain retention of configuration upon solvolysis.[6,10]

Whiting has presented a theory of C–C σ-bond participation for systems in which C–H participation is stereoelectronically forbidden and nucleophilic solvent participation is sterically forbidden. In this theory Whiting states that weak participation can occur without completely protecting the backside from nucleophilic attack (*i.e.*, low retention–inversion ratios), and without rearrangement and rate acceleration.[15] Slightly stronger participation is considered to give higher retention–inversion ratios, small amounts of rearrangement, and no rate acceleration. Only when participation is strong is complete retention, extensive rearrangement, and rate acceleration predicted to occur. On this basis, degrees of participation were assigned to the compounds in Table II.

Whiting's arguments are substantially weakened, in our opinion, by the possibility of retention of con-

Table II. Predictions from Whiting's Hypothesis[a] of Degree of C–C Participation Based on Stereochemistry, Rearrangement, and Rate Acceleration for Tosylate upon Acetolysis

R–OTs	Ret/inv.	% rear product	Rate accel.	Participation
trans,cis-α-Decalyl	0.49	0	None	Weak
2-Adamantyl	2	0.4	None	Slightly stronger
7-Norbornyl	6–19	3	None	Moderate
exo-2-Norbornyl	Large	49.9	Large	Strong

[a] Reference 15.

Table III. Rates and Products for the Aqueous Ethanolysis of Benzhydryl Benzoates at 100°

Substrate	[Ester] $\times 10^3$ [a]	k, sec^{-1}, 70% EtOH[b]	ROEt/ROH[c] (50% EtOH[b])	No. of trials	k_E/k_W	S_{obsd}[d]
3,5-Dinitrobenzoate	0.87	$4.40 \times 10^{-3} \pm 0.06$	1.76 ± 0.17	6	5.64 ± 0.55	0.75
p-Nitrobenzoate	1.05	$5.36 \times 10^{-4} \pm 0.37$	2.14 ± 0.17	18	6.85 ± 0.55	0.84
	1.08		2.06 ± 0.05[e]	3	6.60 ± 0.16	0.82
p-Trifluoromethylbenzoate	1.12	$1.21 \times 10^{-4} \pm 0.03$	1.86 ± 0.13	7	6.15 ± 0.42	0.79
p-Chlorobenzoate	0.86	$1.03 \times 10^{-4} \pm 0.07$	1.94 ± 0.06	6	6.20 ± 0.19	0.79
p-Fluorobenzoate	1.04	$7.02 \times 10^{-5} \pm 0.05$	1.93 ± 0.16	6	6.18 ± 0.51	0.79
p-Methoxybenzoate	0.94	$3.36 \times 10^{-5} \pm 0.12$	2.10 ± 0.22	6	6.72 ± 0.70	0.83

[a] Moles/liter. [b] Volume per cent; determined conductimetrically. [c] Contains 0.012 *M* pyridine. Determined by vpc after 5 half-lives. [d] Log k_E/k_W. [e] 75°.

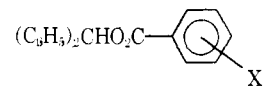
figuration from collapse of solvent-separated pairs, eq 10, and by the additional evidence from our study that 2-adamantyl derivatives solvolyze *via* solvent-separated ion pairs. We view the results of Table II for *trans,cis*-α-decalyl, 2-adamantyl, and 7-norbornyl tosylates as most simply explained in terms of rate-limiting formation of a classical solvent-separated ion pair which is subject to destruction by three competitive pathways: frontside collapse, backside nucleophilic attack, and backside neighboring group attack to give a rearranged carbocation or possibly a nonclassical ion. The parallel trends of increasing retention/inversion and per cent rearranged product (Table II) show that the backside of the reactive carbon is becoming increasingly sterically hindered and thus more susceptible to intramolecular attack by a neighboring C–C band than to backside attack by solvent. Backside solvent attack does not occur on tight ion pairs possibly because this intermediate is far from planar and steric hindrance to nucleophilic approach is still critical; also charge development and therefore "demand" for the nucleophiles electrons is low. Similarly, failure for C–C σ-bond participation at the tight ion pair stage can be rationalized as due to low demand for participation and to the weak nature of participation (because of strain increases) available for *trans,cis*-α-decalyl, 2-adamantyl, and 7-norbornyl intermediates.

We view *exo*-2-norbornyl tosylate as falling in a different class from the other three molecules of Table II. Participation by the 1,6 C–C bond can occur without an increase in strain and is also stereoelectronically feasible. For these reasons participation can occur before the secondary system is forced to ionize and dissociate to the highly unstable solvent-separated ion pair. Thus *exo*-2-norbornyl tosylate is the only compound of Table II which, in our opinion, solvolyzes with neighboring group participation in the rate-determining step.

We regard Whiting's suggestion that neighboring group participation can occur without protecting the backside of the reactive carbon from nucleophilic attack, without rearrangement, and without rate acceleration (when occurring in the rate-determining step) as unjustified. Furthermore, so-called "weak C–C participation" should not be confused with C–C hyperconjugation since attack on a hyperconjugatively stabilized cation must also occur with retention of configuration.[20] It has been emphasized recently that participation with or without bridging is one phenomenon.[21,22]

(20) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

Benzhydryl Benzoates. We have also determined rates and products for the aqueous ethanolysis of a series of benzhydryl benzoates, **7** (Table III). The



7, X = *p*-OCH_3, *p*-F, *p*-Cl, *p*-CF_3, *p*-NO_2, and 3,5-diNO_2

solvolysis products were found not to be stable in the absence of a buffer. Identical product ratios were obtained using 2,6-lutidine or pyridine and pyridine was used in all product determinations. Also, the esters were observed to undergo pyrolysis to alcohols and ethers in the vpc injection port. Product determinations were therefore performed after expiration of 5 half-lives so that essentially all ester had been reacted.

To test for the operation of general base catalysis in the product-determining step of these reactions, we also determined the effect of variations in buffer concentration on the product ratios (Table IV). As can be seen,

Table IV. Effects of Variation in Buffer Concentrations on Product Formation from the Solvolysis of Benzhydryl *p*-Nitrobenzoate at 100° in 70% (v/v) Ethanol

[Ester, *M*] $\times 10^3$	[Pyridine, *M*]	ROEt/ROH[a]	No. of trials
1.38	0.031	3.69 ± 0.34	5
8.46	0.0164	3.42 ± 0.25	3
8.28	0.0232	3.27 ± 0.06	3
9.06	0.0336	3.31 ± 0.16	3

[a] Determined by vpc after 5 half-lives.

buffer concentration has no effect on products, and we conclude these reactions are not subject to general base catalysis.

As can be seen from Table III, the selectivities of the benzhydryl esters are essentially constant despite changes in solvolysis rate and presumably in stability[8] of the resulting intermediates. Thus it *appears* that the products are determined by attack on the free benzhydryl cation. That this is not the case can be deduced from two lines of reasoning. First, there is evidence that all free cations, regardless of structure, have a constant selectivity. In our previous work we have observed log k_E/k_W values for benzhydryl chlorides to be up to 1.04,[8] significantly higher than the presently observed values of approximately 0.80 (Table III). At-

(21) R. Hoffman, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).
(22) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973).

Table V. Products for Solvolysis of Benzhydryl *p*-Nitro- and *p*-Methoxybenzoates in 50, 60, and 70% Aqueous Ethanol at 100°

Substrate	[Ester][a]	[Pyridine][b]	EtOH (v/v), %	k, sec^{-1}	ROEt/ROH[c]	No. of trials	k_E/k_W	S_{obsd}[d]
p-Nitrobenzoate	1.05	0.012	50	5.36×10^{-4}	2.14 (± 0.17)	18	6.85 (± 0.54)	0.84
p-Nitrobenzoate	1.51	0.034	60		2.77 (± 0.17)	3	5.92 (± 0.36)	0.77
p-Nitrobenzoate	1.38	0.026	70		3.46 (± 0.34)	14	4.77 (± 0.47)	0.68
p-Methoxybenzoate	1.09	0.015	50	3.36×10^{-5}	2.10 (± 0.22)	11	6.72 (± 0.70)	0.83
p-Methoxybenzoate	1.06	0.008	60		2.59 (± 0.12)	5	5.54 (± 0.26)	0.75
p-Methoxybenzoate	1.06	0.024	70		3.00 (± 0.36)	5	4.14 (± 0.50)	0.62

[a] m*M*. [b] *M*. [c] Five half-lives. [d] Log k_E/k_W observed.

tack on free benzhydryl cation should give a higher selectivity than that observed.

Product formation by attack on only free cation can be eliminated also by examination of the effects of solvent changes on selectivity. As discussed previously[8] an increase in solvent water content will have no effect on observed selectivity if one intermediate is involved, but if an equilibrium is involved, an increase in solvent water content will cause a shift in the equilibrium and a change in the observed selectivity. We have conducted such an experiment on benzhydryl *p*-nitrobenzoate and *p*-methoxybenzoate (Table V). In these cases an increase in selectivity is observed upon an increase in solvent ionizing power, and product formation by attack on solvent-separated ion pair (III) and free carbocation (IV) is indicated.

Goering and his coworkers have conducted detailed studies of racemization and ^{18}O exchange of benzhydryl benzoates in aqueous acetone.[5,23] Their results are consistent with product formation by attack on solvent-separated ion pair; attack on tight ion pair is indicated not to occur. Additionally, only small amounts of exchange with external benzoate anions were detected, indicating minimal involvement of free carbocation. In contrast, benzhydryl chlorides react in aqueous acetone in large part *via* free carbocations as shown by the occurrence of common ion rate depression and radio-chloride exchange.[3-5,24] Such a result is consistent with greater leaving group ability of chloride relative to benzoates.[25] Our prediction of product formation by attack on solvent-separated ion pair (III) and free carbocation (IV) for aqueous ethanolysis of benzyhydryl benzoates is consistent with these previous results since the aqueous ethanols used in our experiments are more ionizing than the 80 and 90% aqueous acetone used by these workers; an increase in ionizing power of the solvent should increase ion-pair dissociation.[4,6,8]

If the benzhydryl benzoates do undergo aqueous ethanolysis *via* III and IV, there remains one point which must be explained: why does an increase in anion stability (*p*-OCH_3 to 3,5-diNO_2, Table III) not cause a shift in equilibrium and an increase in selectivity? Pyridine is a better nucleophile than ethanol or water.[25] Thus it is possible that the benzoates are attacked first by pyridine to give the unstable benzhydryl pyridinium salt which undergoes attack by ethanol and water to give a constant ether–alcohol ratio, eq 11. The much higher concentrations of

$$(C_6H_5)_2CHX + C_5H_5N \longrightarrow \begin{matrix} \xrightarrow{EtOH} (C_6H_5)_2CHOEt \\ C_5H_5\overset{+}{N}-CH(C_6H_5)_2X^- \\ \xrightarrow[H_2O]{} (C_6H_5)_2CHOH \end{matrix} \quad (11)$$

ethanol and water would seem to eliminate such a possibility. That eq 11 is not operating can be deduced from the following observations. If displacement by pyridine were occurring to any significant extent, it would be in competition with displacement by solvent; changing pyridine concentration should influence this competition, yet no effect is observed (Table IV). Benzhydryl chloride gives a significantly different product ratio from the benzoates in the same pyridine–solvent mixture,[8] thus indicating failure of the process described in eq 11 to dominate solvolysis of the chloride. And finally, use of lutidine rather than pyridine had no effect on product ratios as it should have if attack by the nitrogen base were dominant.

A more likely cause for the product independence of leaving group identity lies in the special nature of water and ethanol solvent-separated ion pairs for esters. As shown in the previous section, for sulfonate anions the water-insulated species (**4**) should be more stable than the ethanol-insulated species (**5**). A similar prediction would seem reasonable for carboxylate ion pairs. Thus as anion stability is increased, there should be a shift in equilibrium from III to IV (increase in a_{IV}, eq 12). Since S_{IV} is indicated from solvent effects (above) to be greater than S_{III}, this shift should result in an increase in observed selectivity, S_{obsd}. However, an increase in anionic stability should also favor formation of the water-separated ion pair over formation of the ethanol-separated ion pair, and in effect *decrease* S_{III} (log k_E/k_W) and thus decrease S_{obsd}. Stated mathematically

$$S_{obsd} = a_{III}S_{III} + a_{IV}S_{IV} \quad (12)$$

and increasing stability of the anion should increase a_{IV} and decrease S_{III}. The failure of S_{obsd} to change with a change in anion stability, despite evidence that an equilibrium is involved, could be due to a fortuitous balancing of an increase in a_{IV} and a decrease in S_{III}; we suggest that this is the case.

Experimental Section

Materials. 2-Adamantyl Arenesulfonates. The arenesulfonates were prepared by reaction of the respective sulfonyl chloride (Aldrich) with 2-adamantanol (Aldrich) in dry pyridine at 0° for 1 week. The esters were then recrystallized from pentane or pentane–ether at −80°: **2-adamantyl *p*-nitrobenzenesulfonate,** mp 146–148° (lit.[26] 144–145°); **2-adamantyl *p*-bromobenzenesulfonate,**

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mp 132–135° (lit.[26] 112.8–113.6°); **2-adamantyl benzenesulfonate,** mp 85–86.2° (lit.[26] 88.2–89.0°); **2-adamantyl *p*-toluenesulfonate,** mp 78.0–79.5° (lit.[26,27] 82.1–82.5°, 82.7–83.7°); **2-adamantyl *p*-methoxybenzenesulfonate,** mp 60.0–61.5° (lit.[26] 62.7–63.2°).

Benzhydryl Benzoates. These compounds were prepared by reacting a mixture of the benzoyl chloride (approximately 10% excess) (Aldrich), benzhydrol, and a minimum amount for solution of dry pyridine at 5° for 4 hr and then at −20° for 18 hr. The pyridine solution was poured into ice and water and extracted twice with ether, and this solution was dried. The usual[28] acid wash to remove pyridine was omitted. The esters were then recrystallized from pentane. All esters gave satisfactory nmr and ir spectra and the two of the series examined gave satisfactory analyses: **benzhydryl 3,5-dinitrobenzoate,** mp 137.5–141.0°; **benzhydryl *p*-nitrobenzoate,** mp 133–134° (lit.[29] 133.4–134.0°) (*Anal.* Calcd: C, 72.03; H, 4.54. Found: C, 72.00; H, 4.64); **benzhydryl *p*-trifluoromethylbenzoate,** mp 93.5–95.0°; **benzhydryl *p*-fluorobenzoate,** mp 80.5–82.5°; **benzhydryl *p*-chlorobenzoate,** mp 86.5–88.0°; **benzhydryl *p*-methoxybenzoate,** mp 96.0–98.0° (*Anal.* Calcd: C, 79.22; H, 5.70. Found: C, 79.12; H, 5.80).

Ethanol was distilled from magnesium ethoxide.

Pyridine was distilled and stored over potassium hydroxide pellets.

Kinetic Procedure. Rates were determined conductimetrically as previously described.[11]

Product Determination. Product ratios were determined by direct gas chromatographic analysis of reaction mixtures. A 6 ft × 1/8 in. column packed with SF96 on 60–70 mesh Anakrom ABS was used.

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Effect of Polyelectrolytes upon the Kinetics of Ionic Reactions. IV. The Decomposition of Aspirin in Aqueous Solutions Containing Polycations

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Abstract: The decomposition of aspirin in aqueous solutions of cationic polyelectrolytes has been studied over a considerable pH range (1.5–11.0). Poly(ethylenimine), a weak polyelectrolyte containing free amino groups which act as nucleophilic reagents upon the substrate, and the strong polyelectrolyte poly(vinylbenzyltrimethylammonium chloride), without such reactive groups in its molecule, were employed in the present study. Poly(vinylbenzyltrimethylammonium chloride) was found to modify only slightly the rate of hydrolysis of aspirin in the pH independent region (5–9), but it increases by a factor of 9 the rate of bimolecular saponification of the ester in alkaline solutions. This acceleration can be explained satisfactorily with an electrostatic model which predicts an enhanced local concentration of the substrate anion and OH^- near the chains due to the large charge density of the polymeric chains. On the other hand, in poly(ethylenimine) solutions the rate of decomposition of aspirin is substantially increased, passing through a maximum at pH 7.8, where the rate constant is 1275 times greater than in the absence of polyelectrolyte. A further increase in pH causes a decrease in rate constant until the value corresponding to solutions without polyelectrolyte is reached at pH ~11. The explanation of this behavior is given in terms of two competing effects. When the pH increases, the fraction of amino groups which are free increases also, thus enhancing the possibility of nucleophilic attack on the substrate; on the other hand, the concomitant decrease of charged groups on the macroion reduces the local concentration of the charged substrate near the polymeric chain.

It has been shown[2,3] that the rate of decomposition of *p*-nitrophenyl phosphate (NPP) is modified by the presence of polycations in the solution. The observed effect depends on the pH of the solution and on the nature of the polycations. When the polyelectrolyte was poly(ethylenimine) (PEI), which has groups capable of acting as nucleophilic reagents, the rate of decomposition was substantially increased. For polyions like poly(vinylbenzyltrimethylammonium chloride) (PVBA-Cl), having no reactive groups, the rate of hydrolysis at those pH values where the mechanism of hydrolysis is known to be unimolecular was found to be higher than in water. It was conclusively shown that these modifications of the rate of decomposition of NPP depend on the existence of a high charge density on the macroions; *i.e.*, it is a manifestation of the so-called polyelectrolyte effect.

Klotz and coworkers[4] and Overberger and coworkers[5] have studied a large number of reactions in solution in the presence of added polymeric solutes; in general their macromolecules had groups capable of reacting with the substrates, and with a proper selection of these groups the effect of polymers on the reactions can be very large. In polyionic solutions the reactions between the reactive groups on the macroions and oppositely charged substrates may be considered affected by two

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