Product Analysis. To 100 ml of 10^{-4} *M* $HClO_4$ was added 8.61 g of **1** at room temperature. After 2 hr the solution was extracted with five 50-ml portions of ether. The ether was removed, leaving 6.76 g of residual liquid. Analysis of the residue by glc showed one major component (95%), water, methanol, and a minor component (1.5%) judged to be the dimethyl acetal of **2** by comparative retention times.

The major component was identified as 2-ethyl-2-hydroxybutanal: bp 59–60° (26 mm); $\delta_{TMS}^{C_3D_6O}$ 0.8 (t, *J* = 7 Hz, 6 H), 1.8 (m, 4 H), 4.2 (br s, 1 H, O*H*), 9.51 (s, 1 H, C*H*O); ν^{neat} 3450, 2720 (sh), and 1720 cm^{-1}; mass spectrum 116 (parent), 45 (base).

Anal. Calcd for $C_6H_{12}O_2$: C, 62.02; H, 10.43. Found: C, 61.84, 61.99; H, 10.30, 10.36.

Kinetic Procedure. All kinetic measurements were carried out by monitoring the formation of aldehyde product at 290 nm (ϵ 21) or ketone product at 316 nm. The solvent used throughout was 10% dioxane–water (v/v) with μ maintained at 0.11 by $NaClO_4$ except as noted below. Buffers employed were perchloric acid (pH 3.41–4.81), formic acid (pH 3.86–4.75), acetic acid (pH 4.09–6.12), cacodylic acid (pH 5.65–7.07), and triethanolamine (pH 6.96–7.61). A 0.5 *M* stock solution of DOAc in D_2O (99.8%), prepared according to Goodall and Long,[35] was used to make up acetate buffers in 10% dioxane–D_2O (v/v). The pH meter readings were converted to pD values by adding 0.4.[36] A Radiometer Model 4 pH meter was used to determine the pH values of buffer solutions.

Reactions were started by adding 14 μl of **1** or 1.5 μl of **4** to 3 ml of a buffer solution at 25.0° in a 1-cm silica cell, shaking vigorously and replacing in the thermostated (25.0 ± 0.1°) cell compartment of a Beckman DU-2 spectrophotometer. The reactions were followed to 60–80% of completion; infinity readings were taken after 8–12 half-lives. Pseudo-first-order rate constants, k_{obsd}, were calculated by means of a computer program which utilizes a variable infinity point.[37] Swinbourne's method[38] was used as a check; satisfactory agreement between the two methods was realized in all cases.

The first-order rate constant in a solution containing an $HA-A^-$ acid–base pair was taken as

$$k_{obsd} = k_{H_2O} + k_Ha_H + k_{OH}a_{OH} + k_{HA}[HA] + k_A[A^-]$$

The rate constants k_H and k_{H_2O} were obtained from the least-squares slope and intercept, respectively, of plots of log k_{obsd} *vs.* $[HClO_4]$. Plots of k_{obsd} *vs.* [HA] at three different pH values give slopes from which may be extracted k_{HA} and k_A and intercepts which yield k_{OH}. Linear least-squares analysis was applied throughout.

Activation parameters were obtained from plots of log k_H or log k_{H_2O} *vs.* $1/T$. The temperatures, 15.0, 25.0, 30.0, and 35.0°, could be controlled to ±0.1°.

Acknowledgments. We gratefully acknowledge the support of the National Science Foundation through Grants GP-7392 and GP-14693. Computer time was donated by the University of Hawaii Computing Center. Sherwin Amimoto assisted with the computer program.

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[36] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

[37] The program is a least-squares modification of one originally given by K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, Chapter 9.

[38] E. S. Swinbourne, *J. Chem. Soc.*, 2371 (1960).

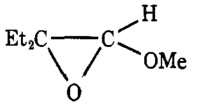
Kinetics and Mechanism of Epoxy Ether Hydrolysis. II. Mechanism of Ring Cleavage[1]

Arthur L. Mori[2] and Larry L. Schaleger*

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822. *Received November 29, 1971*

Abstract: The kinetics of ring cleavage of two epoxy ethers, 1-methoxy-2-ethyl-1,2-epoxybutane (**1**) and 1-methoxy-1-phenyl-2-methyl-1,2-epoxypropane (**2**), have been studied in 10% aqueous dioxane (v/v) at 25° and pH 8–13. Both substrates hydrolyze *via* pH-independent and H_3O^+-catalyzed reactions. General acid catalysis by $H_2PO_4^-$ is observed in the hydrolysis of **2**. Solvent deuterium isotope effects, k_D/k_H, for catalysis by L_3O^+ are 2.02 for **1** and 1.35 for **2**. Entropies of activation are −11 eu for **1** and −15 eu for **2**. Compound **2** reacts 10.2 times slower than **1**. These results suggest that proton transfer to ring oxygen is concerted with C–O bond breaking in relatively reactant-like transition states. The pH-independent cleavage of **1** has $k_{D_2O}/k_{H_2O} = 0.53$ and $\Delta S^{\ddagger} = -49$ eu. Catalysis by hydroxide ion is also observed although k_{OH}/k_{H_2O} is only 11 M^{-1}. The corresponding parameters for **2** are $k_{OH}/k_{H_2O} = 0.35$ and $\Delta S^{\ddagger} = -36$ eu. A bimolecular mechanism is proposed in which nucleophilic attack is concerted with proton transfer.

The hydrolysis of 1-methoxy-2-ethyl-1,2-epoxybutane (**1**) undergoes a change of mechanism in 10% aqueous dioxane (v/v) at 25° at a pH of ~8.0. The low pH reaction has been characterized[3] as the hydrolysis of the hemiacetal intermediate, $Et_2C(OH)CH(OCH_3)OH$. We turn now to the high pH reaction which involves rate-determining cleavage of the epoxide ring. The kinetics of the ring opening of 1-phenyl-2-methyl-1,2-epoxypropane (**2**) are also reported.



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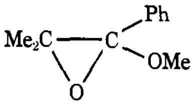

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Epoxy ether **1** is an acetal; **2** is a ketal. Simple acetals and ketals generally hydrolyze *via* an A1 mechanism, *i.e.*, equilibrium protonation of oxygen followed by rate-determining dissociation of ROH to give a carboxonium ion.[4] However, recent work has demonstrated that the normal A1 mechanism can be modified by appropriate structural alteration.[5–9] The

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[1] Based in part on the Ph.D. Thesis of A. L. M., University of Hawaii, 1971.

[2] NSF Academic Year Participant, 1967–1968; NSF Trainee, 1968–1971.

[3] A. L. Mori, M. A. Porzio, and L. L. Schaleger, *J. Amer. Chem. Soc.*, **94**, 5034 (1972).

[4] E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967).

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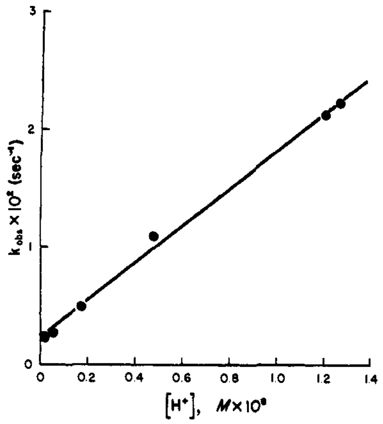


Figure 1. Plot of k_{obsd} *vs.* a_H, the activity of hydrogen ion, for the hydrolysis of 1-methoxy-2-ethyl-1,2-epoxybutane (**1**) at 25° in 10% aqueous dioxane and pH 8.2–10.7.

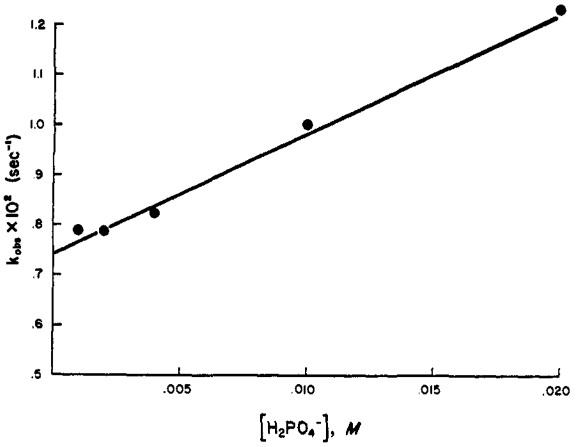
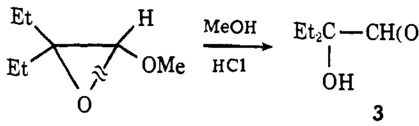


Figure 2. Plot of k_{obsd} *vs.* concentration of dihydrogen phosphate ion for hydrolysis of 1-methoxy-1-phenyl-2-methyl-1,2-epoxypropane (**2**) at 25° in 10% aqueous dioxane. The nonzero slope is evidence of buffer catalysis.

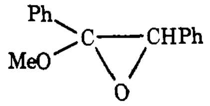
major factors involved appear to be ease of C–O bond breaking, substrate basicity, and relative carboxonium ion stability. The incorporation of one oxygen of an acetal into a three-membered ring was expected to affect all three factors, and the relationship of this structural change to mechanisms of hydrolysis forms the subject of this paper.

Results

The product of hydrolysis of **1** at pH 10, as at pH 4, is 2-ethyl-2-hydroxybutanal. The direction of ring opening was determined to involve C(1)–O cleavage by the observation that the product of methanolysis is the dimethyl 2-hydroxyacetal (**3**). Analogous results have been obtained previously for the opening of the epoxides **2**,[10] **4**,[11,12] and **5**[13] in neutral and/or basic methanol as well as in acidic alcohol solutions. Breaking of the C(1)–O bond appears, therefore, to be the exclusive mode of ring cleavage in the epoxy ether series, irrespective of substitution.



1 **3**



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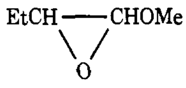

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Pseudo-first-order rate constants for the hydrolysis of **1** and **2** at pH 8.2–10.7 in triethanolamine, methyldiethanolamine, and 2,2,6,6-tetramethyl-4-piperidinol buffers are given by eq 1, where $\log a_H = -\text{pH}$. Plots

$$k_{obsd} = k_H a_H + k_{H_2O} \qquad (1)$$

of k_{obsd} *vs.* a_H, as shown in Figure 1, yield slopes, k_H, and intercepts, k_{H_2O}. Neither epoxy ether showed detectable buffer catalysis with these buffers. However, **2** was subject to catalysis by $H_2PO_4^-$ as shown in Figure 2.

Solvent deuterium isotope effects on the cleavage of **1** are $k_D/k_H = 2.02 \pm 0.11$ and $k_{D_2O}/k_{H_2O} = 0.53 \pm 0.04$. Corresponding values for **2** are $k_D/k_H = 1.35 \pm 0.06$ and $k_{D_2O}/k_{H_2O} = 0.35 \pm 0.02$. Changing the solvent from 10 to 50% aqueous dioxane (v/v) was found to slow down the pH-independent hydrolysis of **1** by a factor of 14. These rate data are collected in Table I.

Table I. Rate Constants for Epoxy Ether Hydrolysis at 25° and μ = 0.11 (with NaClO$_4$)

% dioxane (v/v)	Buffers[a]	Catalyst	k^b (errors[c])
	1-Methoxy-2-ethyl-1,2-epoxybutane (**1**)		
10	A, B, C	H_3O^+	$1.61\ (\pm 0.03) \times 10^6$
10	A, B, C	H_2O	$2.15\ (\pm 0.07) \times 10^{-3}$
10	C–0.06 M NaI	H_2O	$2.23\ (\pm 0.04) \times 10^{-3}$
10	D	D_3O^+	$3.25\ (\pm 0.17) \times 10^6$
10	D, E, F	D_2O	$1.14\ (\pm 0.06) \times 10^{-3}$
50	G	H_2O	$1.51\ (\pm 0.04) \times 10^{-4}$
	1-Methoxy-1-phenyl-2-methyl-1,2-epoxypropane (**2**)		
10	A, B, C	H_3O^+	$1.57\ (\pm 0.06) \times 10^5$
10	A, B, C	H_2O	$1.07\ (\pm 0.05) \times 10^{-5}$
10	H	$H_2PO_4^-$	$2.38\ (\pm 0.18) \times 10^{-1}$
10	F	D_3O^+	$2.12\ (\pm 0.04) \times 10^5$
10	F	D_2O	$3.79\ (\pm 0.09) \times 10^{-6}$

[a] A, triethanolamine, pH 7.92; B, methyldiethanolamine, pH 7.90–8.77; C, 2,2,6,6-tetramethyl-4-piperidinol, pH 9.26–10.70; D, triethanolamine-d_3, pD 8.22–8.98; E, methyldiethanolamine-d_2, pD 8.50; F, 2,2,6,6-tetramethyl-4-piperidinol-d_2, pD 10.52–11.14; G, 2,2,6,6-tetramethyl-4-piperidinol, pH 9.79; H, phosphate, pH 7.32. [b] Units, M^{-1} sec^{-1} (H_3O^+, D_3O^+, and $H_2PO_4^-$ reactions) or sec^{-1} (H_2O and D_2O reactions). [c] These are probable errors obtained by least-squares analysis of eq 1.

Activation parameters for the cleavage of **1** and **2**, given in Table II, were obtained by linear least-squares regression analysis of log k *vs.* $1/T$ data for runs at 25, 35, and 45°. These Arrhenius plots are shown in Figure 3.

The hydrolysis kinetics of **1** were also investigated in 0.010–0.174 M NaOH solutions. A specific hydroxide ion catalyzed reaction became apparent at about 0.05

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(10) T. I. Temnikova and N. I. Almashi, *Zh. Obshch. Khim.*, **23**, 1338 (1953); *Chem. Abstr.*, **48**, 12025b (1954).

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Table II. Activation Parameters for Hydrolysis of Epoxy Ethers **1** and **2** at 25° in 10% Aqueous Dioxane (v/v), $\mu = 0.11$ (with $NaClO_4$)

Substrate	Catalyst	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
1	H_3O^+	5.6 ± 0.4	-11 ± 1
1	H_2O	6.4 ± 0.2	-49 ± 1
1	H_2O^a	14.9 ± 0.1	-26 ± 1
2	H_3O^+	5.9 ± 0.2	-15 ± 1
2	H_2O	13.6 ± 0.3	-36 ± 1

[a] Solvent was 50% aqueous dioxane (v/v).

M NaOH and a rate constant, k_{OH}, of about 2×10^{-2} M^{-1} sec^{-1} (±30%) was obtained. These results are given in Table III. The accuracy of these experiments was limited because of time-dependent infinity readings, possibly the result of a subsequent Cannizzaro reaction of the aldehyde product.

Table III. Kinetics of Hydrolysis of **1** in Sodium Hydroxide Solutions (10% Aqueous Dioxane) at 25°

[NaOH], *M*	$10^3 k_{obsd}$, sec^{-1}	$(k_{obsd}{}^a - k_{H_2O})/[OH]$, M^{-1} sec^{-1}
0.0100	1.84 ± 0.04	
0.0250	2.14 ± 0.04	
0.0625	3.29 ± 0.20	1.8×10^{-2}
0.104	4.18 ± 0.02	2.0×10^{-2}
0.174	4.31 ± 0.06	1.2×10^{-2}

[a] $k_{H_2O} = 2.15 \times 10^{-3}$ sec^{-1}.

Discussion

The normal A1 mechanism of acetal hydrolysis is generally characterized by specific hydronium ion catalysis, solvent deuterium isotope effects, k_D/k_H, of greater than 2.5, and entropies of activation around zero or positive.[4] The kinetic parameters for epoxy ether hydrolysis are clearly different from those expected for an A1 mechanism.

The role of basicity in determining mechanisms of acetal hydrolysis has been pointed out by Bunton and DeWolfe.[14] It has been shown that oxiranes and aziridines are anomalously weak bases toward the proton.[15] Since the pK_a of ethylenimine[16] is 3 log units less than that of dimethylamine, one might suppose that a similar difference would hold between ethylene oxide and dimethyl ether,[17] putting the pK_a of the conjugate acid of ethylene oxide at about −6. Substituent effects may then be estimated taking ρ^* as −3 and polar substituent constants, σ^*, for OMe, Me (or Et), and C_6H_5 as 0.52, −0.10, and +0.215, respectively.[14] This leads to pK_a values of −7 for **1** and −7.6 for **2**. These may be compared with values calculated as above or obtained by means of hydrogen bond strength determination: 2,2-dimethoxypropane,[18] −5.2; para-substituted benzaldehyde diethyl acetals,[18] −5.7; methyl orthoacetate,[18] −6.5; and ethyl orthobenzoate,[14] −7.6.

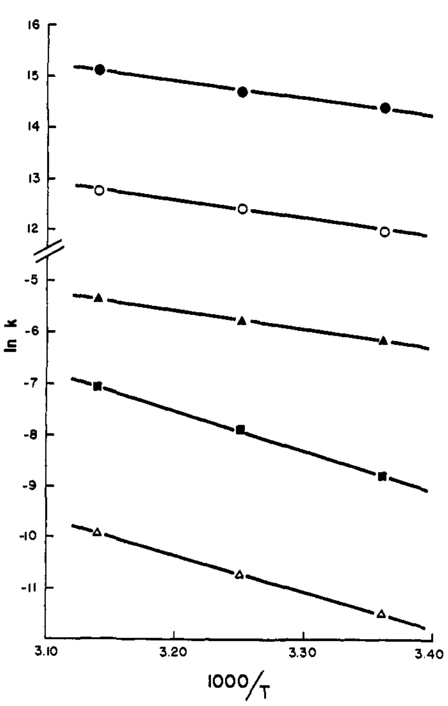

Figure 3. Arrhenius plots for the hydrolysis of **1** catalyzed by H_3O^+ (●) and by H_2O (▲) in 10% aqueous dioxane and by H_2O (■) in 50% aqueous dioxane. Also shown are the corresponding lines for the hydrolysis of **2** catalyzed by H_3O^+ (○) and by H_2O (△).

The overall rate constant k_r for an A1 mechanism is given by k_2/K_a where $K_a = k_{-1}/k_1$. Given that K_a is 10^7 *M* and k_r, 1.6×10^6 M^{-1} sec^{-1}, a value of $>10^{13}$ sec^{-1} for k_2, formation of the carboxonium ion intermediate, is obtained. Since this is greater than the diffusion-controlled limit for the reverse of the protonation step, a simple A1 mechanism is eliminated as a possibility, thus strengthening the conclusion reached on the basis of entropies and solvent deuterium isotope effects.

A second structural factor, facilitation of C–O bond breaking, is manifested in relief of bond angle strain upon ring cleavage. The strain energy of the oxirane ring has been put at 21.5[19] and 28[20] kcal mol^{-1}.

The rate constant, k_H, for the hydrolysis of **1** is some 6–8 powers of 10 greater than those for similarly substituted open-chain acetals.[21] This rate enhancement must be due primarily to destabilization of the ground state relative to the partially ring-opened transition state.

These two factors, bond angle strain and, to a lesser degree, basicity, alter the energy profile for epoxy ether hydrolysis relative to acetal hydrolysis as diagrammed schematically in Figure 4. Whereas proton transfer is complete and carboxonium ion formation is rate determining in the case of acetal hydrolysis,[4] the destabilization of ground state (E) relative to carboxonium ion (R^+) and of protonated ground state (EH^+) relative to E can be expected to cause the transition state in epoxy ether hydrolysis to be more reactant-like.

The solvent deuterium isotope effect, k_D/k_H, of 2.02 may be compared with a mean value of 2.8 for simple

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(14) C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, **30**, 1371 (1965).

(15) M. Brandon, M. Tamres, and S. Searles, Jr., *J. Amer. Chem. Soc.*, **82**, 2932 (1960), and references cited therein.

(16) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *ibid.*, **78**, 4917 (1956).

(17) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(18) T. Pletcher and E. H. Cordes, *J. Org. Chem.*, **32**, 2294 (1967).

(19) R. Ketcham and V. P. Shah, *J. Chem. Eng. Data*, **11**, 106 (1966).

(20) J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

(21) The specific 25° rate constant k_H, for hydrolysis of $Et_2C(OH)CH(OMe)_2$, is estimated[3] to be 0.01 M^{-1} sec^{-1}.

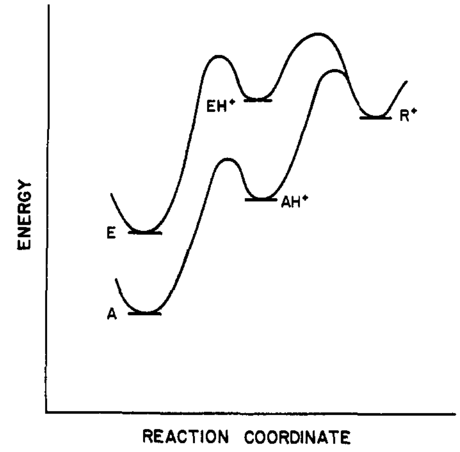


Figure 4. Probable reaction coordinate diagram for hydrolysis of an epoxy ether (E) such as **1** and an acetal (A) such as $Et_2C(OH)CH(OMe)_2$, both giving rise to the same carboxonium ion intermediate (R^+). EH^+ and AH^+ represent the respective acids.

acetals,[4] suggesting that proton transfer is well advanced but not complete in the transition state for the hydrolysis of **1**. The fact that the phenyl-substituted epoxy ether **2** reacts slower suggests that C–O bond breaking lags well behind O–H bond making in the transition state.[5]

The mechanism of the hydronium ion catalyzed reaction therefore appears to involve partially rate-determining proton transfer concerted with but running ahead of C–O bond cleavage. The possibility that reaction is further assisted by water acting as a nucleophile cannot be excluded. The negative entropies of activation are consistent with a bimolecular rate-determining step.

The pH-independent reaction features a large negative entropy of activation and a solvent deuterium isotope effect, k_{H_2O}/k_{D_2O}, of about 0.5. Fife[22] and Salomaa[23] have discovered several examples of pH-independent acetal hydrolysis, all of which are characterized by entropies of activation which are close to zero and solvent deuterium isotope effects around unity. These have been considered to be unimolecular decompositions. The pH-independent hydrolyses of **1** and **2** are evidently bimolecular.

Table IV compares entropies of activation, solvent deuterium isotope effects, and k_{OH}/k_{H_2O} ratios for the "spontaneous" hydrolyses of a number of oxygenated substrates. The reactions selected are all presumed to be of the bimolecular type with water acting as a nucleophile and/or proton transfer agent. The pH-independent hydrolysis of ethylene oxide, a good model for simple S_N2 displacement, is only 10% faster in H_2O than in D_2O.[24] Thus, the likelihood that **1** and **2** hydrolyze by the same pathway is remote. Ethylene oxide is also 15 times more sensitive to attack by OH^- than **1**.[25,26] The relative insensitivity of **1** to hydroxide ion catalysis suggests that nucleophile–substrate interaction is quite weak in the transition state. This accounts for our inability to detect nucleophilic catalysis of the hydrolysis of **1** in the presence of 0.06 *M* NaI (see Table I).

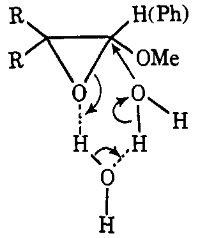
Table IV. Comparative 25° Kinetic Parameters for Selected Spontaneous Hydrolyses

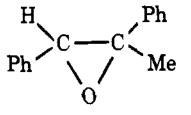
Reactant	$\Delta S^{\ddagger}$, eu	k_{H_2O}/k_{D_2O}	k_{OH}/k_{H_2O}, M^{-1}
1. Ethylene oxide	-24^a	1.1^b	160^a
2. Acetic anhydride	-35^c	2.9^d	
3. **1**^{e}	-49 (-26^f)	1.9	11
4. **2**^{e}	-36	2.8	
5. $Et_2C(OH)CH(OCH_3)OH^g$	-31	1.7	10^8

[a] Reference 26. [b] Reference 24. [c] A. R. Butler and V. Gold, *J. Chem. Soc.*, 2305 (1961). [d] C. A. Bunton, N. A. Fuller, S. G. Perry, and V. J. Shiner, *ibid.*, 2918 (1963). [e] This work. [f] 50% aqueous dioxane (v/v). [g] Reference 3.

The pH-independent reactions of **1** and **2** seem rather better placed among a class exemplified by the hydrolysis of acetic anhydride. These reactions evidently involve a large number of solvent molecules with proton transfer occurring in the rate-determining step.

Fife and Brod have noted[22] that the unimolecular mechanism of pH-independent acetal hydrolysis appears to require either the combination of a good leaving group and a reasonably stable carbonium ion or an exceptionally stable carbonium ion. Thus, it is somewhat surprising to find that both **1** and **2** eschew the unimolecular in favor of a complex bimolecular process. It is possible however that the geometry of the three-membered ring facilitates unhindered front-side attack by a water molecule(s) hydrogen bonded to ring oxygen. There is precedent for front-side attack in that a number of di- and trisubstituted oxiranes such as **6** and **7** are known to react with nucleophiles to give the products of retained configuration.[27]





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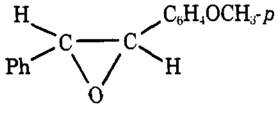

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The bimolecular mechanism may also be favored due to activation toward nucleophilic attack by the methoxyl group.[28] However, the exact nature of this effect remains somewhat obscure.

Experimental Section

Materials. The substrates **1** and **2** were prepared as previously described.[3] The buffer amines, triethanolamine, methyldiethanol-

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(22) T. H. Fife and L. H. Brod, *J. Amer. Chem. Soc.*, **92**, 1681 (1970)

(23) P. Salomaa, *Suom. Kemistilehti B*, **37**, 86 (1964).

(24) J. G. Pritchard and F. A. Long, *J. Amer. Chem. Soc.*, **78**, 6008 (1956).

(25) This calculation takes k_{OH}/k_{H_2O} as the measure of sensitivity.

(26) P. O. I. Virtanen, *Ann. Acad. Sci. Fenn. Ser. A2*, No. **124**, 1 (1963).

(27) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(28) The activating effect of an α-methoxyl group in bimolecular nucleophilic displacement reactions is of the order of 10^3–10^5; see A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 26.

amine, and 2,2,6,6-tetramethyl-4-piperidinol, were purchased from Aldrich Chemical Co. and used as received. All buffer solutions were 10% aqueous dioxane (v/v); an ionic strength of 0.11 was maintained with $NaClO_4$. Deuterium oxide (99.8%) was purchased from Columbia Organic Chemicals. The pK_a of 2,2,6,6-tetramethyl-4-piperidinol was estimated to be 10.0 from the **pH** of a 1:1 buffer solution in 10% dioxane (μ = 0.11).

Product Analysis. I. Methanolysis. To 50 ml of absolute methanol into which HCl gas had been bubbled was slowly added 5.00 g (0.038 mol) of **1** at ice-bath temperature. The solution was allowed to warm to 30°, neutralized with dilute aqueous NaOH, and extracted with four 40-ml portions of ether, and the combined ethereal extracts were dried over $MgSO_4$. Removal of ether under reduced pressure left a residue (4.51 g) which was distilled to yield 2.42 g of 2-ethyl-2-hydroxybutanal dimethylacetal: bp 64–65° (8 Torr); n^{25}D 1.4214; $\delta_{TMS}^{CCl_4}$ 1.0 (t, 6 **H**), 1.7 (q, 4 H), 2.5 (br s, –OH), 4.1 (s, 6 H), 4.8 (s, 1 H).

Anal. Calcd for $C_8H_{18}O_3$: C, 59.2; H, 11.2. Found: C, 59.1; H, 11.1.

II. Hydrolysis. The hydrolysis product of **1** at pH 10 was determined to be 2-ethyl-2-hydroxybutanal as previously described[3] for hydrolysis at pH 4. A 60% yield of material shown by gc to be 95% pure aldehyde was obtained.

Kinetic Procedures. These have been described.[3] Rate measurements at 25, 35, and 45° (±0.1°) were used to calculate activation parameters. Kinetic runs in all buffer solutions were strictly first order to 60–75% completion.

Acknowledgments. We gratefully acknowledge support of this work by the National Science Foundation through Grants GP-7392 and GP-14693. We thank the University of Hawaii Computer Center for the donation of computer time. We are indebted to Sherwin Amimoto for assistance with computer programs. Dr. Michael A. Porzio first synthesized the epoxy ethers used in this work and carried out the methanolysis product analysis.

Structural Effects in Solvolytic Reactions. V. Rates and Products in the Acetolysis of Substituted *cis*-2-Phenylcyclopentyl Tosylates and Deuterium Tagged Derivatives. Nature of the Reaction Pathway in the Absence of Aryl Participation[1]

C. J. Kim[2] and Herbert C. Brown

Contribution from the Richard B. Wetherill Laboratory,
Purdue University, Lafayette, Indiana 47907. *Received September 29, 1971*

Abstract: A series of substituted *cis*-2-phenylcyclopentyl tosylates was prepared and the rates and the products of acetolysis were studied. The rate data reveal the absence of aryl participation, and the product data show no evidence for the incursion of aryl-bridged species as intermediates. Thus, the aryl-assisted pathway is effectively absent in the present system. This provides us with a representative secondary β-arylalkyl system in which the solvolysis proceeds *via* aryl-unassisted pathways only. A study of the deuterium tagged derivatives, *cis*-2-phenylcyclopentyl-*1*-d_1 tosylate and the *2*-d_1 isomer, revealed that a predominant portion of the product arises from a rearranged tertiary arylic cation. This indicates that the solvolysis pathway in the present system is characterized largely by a process involving hydride shift. However, the rates of solvolysis reveal very little effect of increasing stability of the tertiary benzylic cation center arising from the effect of activating substituents in the aromatic ring. This suggests that the first intermediate cannot be the tertiary cation. Consequently, the solvolysis is interpreted in terms of a mechanism involving the formation of a tight ion pair as the first intermediate.

The acetolysis or formolysis of secondary alkyl arenesulfonates was originally suggested by Winstein and his coworkers to be nearly limiting.[3,4] This position, which postulates the rate-determining formation of carbonium ion intermediates with little nucleophilic solvent participation, has received general acceptance.[6–12]

In line with this interpretation, the phenyl-unassisted process in the acetolysis or formolysis of secondary β-phenylalkyl arenesulfonates was first characterized by Cram with such terms as S_N1 and E1.[13] At the same time, however, the term "solvent participation in the ionization step," has also been used to describe the ionization process to "solvated" open ions,[14] a process

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[1] For a preliminary report, see C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4286 (1969).

[2] Postdoctoral research associate, 1968–1970, on a grant (GP 6492 X) supported by the National Science Foundation.

[3] Although the classic Ingold's scheme defines the solvolysis of secondary derivatives as borderline,[5] it was suggested[4] that a secondary system involving a tosyloxy group, a far better leaving group than halogen, and a solvent of low nucleophilicity, such as acetic acid or formic acid, would approach a limiting mechanism in character.

[4] (a) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 828, 846 (1948); (b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952); (d) S. Winstein and N. J. Holness, *ibid.*, 77, 5562 (1955).

[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[6] (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[7] E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 105.

[8] M. C. Whiting, *et al.*, *J. Chem. Soc. B*, 355, 365 (1968).

[9] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1966).

[10] H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

[11] W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962).

[12] See also: (a) J. D. Roberts, W. Bennett, R. E. McMahon, and E. W. Holroyd, Jr., *J. Amer. Chem. Soc.*, **74**, 4283 (1952); (b) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954); (c) J. O. Stoffer and J. D. Christen, *ibid.*, **92**, 3190 (1970).

[13] (a) D. J. Cram, *ibid.*, **74**, 2129 (1952); (b) *ibid.*, **74**, 2137 (1952); (c) *ibid.*, **74**, 2159 (1952); (d) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953).

[14] Such species were usually depicted with structures which have dotted line(s) between the carbonium center and solvent molecule(s).[16,17]