Cyclopropylcarbinyl β-Naphthalenesulfonate Solvolysis. Solvolytic Behavior Study

DONALD D. ROBERTS

Department of Chemistry, Louisiana Polytechnic Institute, Ruston, Louisiana 71270

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The activation parameters for the solvolysis of cyclopropylcarbinyl (**3**-ONas) and cyclobutyl (**4**-ONas) β-naphthalenesulfonate have been determined in acetic acid and ethanol. The variable partitioning of the activation parameters is discussed in terms of data for related substrates. The solvolysis rates of crotyl β-naphthalenesulfonate have been determined in a series of solvents of varying ionizing strength. The correlation of the crotyl β-naphthalenesulfonate solvolysis rates with those of cholesteryl tosylate gives further support for this solvent LFE relationship. Kinetic salt effects on solvolysis of **3**-ONas and **4**-ONas were studied. The effect of first-order salt effects on internal-return isomerization of **3**-ONas is discussed.

In our study[1] of substituent effects upon the rates of solvolysis of cyclopropylcarbinyl arenesulfonates, **3**, it has become increasingly apparent that the mode of charge dispersal in the first formed cationic intermediate varies with substitution.

In view of this hypothesis and prompted by activation parameter studies[2] it was suggested[3] that the reaction medium influenced the transition state geometry of unsubstituted cyclopropylcarbinyl derivatives. However, some doubt exists as to the accuracy of the kinetic data due to the presence of internal-return isomerization and the use of **3** tosylate, a liquid starting material, too unstable to purify by distillation.

This uncertainty is eliminated by use of crystalline β-naphthalenesulfonate esters, and in this paper we report the solvolytic behavior of the β-naphthalenesulfonate esters of cyclopropylcarbinol (**3**-ONas) and cyclobutanol (**4**-ONas). In the course of this investigation some related points of interest developed and are included in this report.

Results

Rate measurements were determined by titration of liberated acid and are given in Table I along with associated activation parameters. The apparent first-order rate constants, k_t, were computed on the basis of acid infinity titer and, therefore, are a sum of the rearrangement, k_R, and the solvolytic, k_s, rate constants ($k_t = k_R + k_s$) for those solvolysis reactions accompanied by internal-return isomerization.[4] The ethanolysis of **3**-ONas, contrary to expectation,[5,6] was accompanied by internal-return isomerization (even in the presence of urea) although of decreased magnitude relative to acetolysis. This decrease in internal-return isomerization with increasing solvent nucleophilicity is in accord with previous findings.[7] It is noted, however, that k_R represents only part of the value for k_{-1}, the rate of internal return, since recombination without rearrangement remains undetected. To the extent that a common cationic intermediate is involved in both the reaction with solvent and the recombination with anion, one can estimate that k_{-1}/k_s is 4.0 for acetolysis of **3**-ONas and 0.4 for ethanolysis. These values are comparable to those reported[8] for solvolysis of secondary allyl chlorides.

The recorded $\Delta H^{\pm}$ and $\Delta S^{\pm}$ values for the acetolysis of **3**-ONas were computed on the basis of a nine-point regression analysis over a 23° temperature range and are in excellent agreement with previously reported[2] values for **3** benzenesulfonate, **3** tosylate, and **3** *p*-methoxybenzenesulfonate.

The data of Table II, which relate to substrates that undergo anchimerically assisted ionization reactions, emphasize the anomolous partitioning of the activation parameters for the solvolysis of **3**-ONas. It is readily apparent that the $\Delta S^{\pm}$ value for the acetolysis of **3**-ONas is much more negative than that obtained for related substrates. Furthermore, the $\Delta S^{\pm}$ values for ethanolysis of structurally related cyclobutyl β-naphthalenesulfonate or 1-methylcyclopropylcarbinyl tosylate are decreased relative to the acetolysis values while the $\Delta S^{\pm}$ value for ethanolysis of **3**-ONas exhibits a contrasting increase.

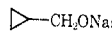
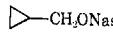
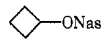
Since the $\Delta S^{\pm}$ values for the solvolysis of *p*-methoxyneophyl and cholesteryl tosylate are nearly invariant to this solvent change, it is unlikely that the nonparallel behavior of $\Delta S^{\pm}$ for 1-methylcyclopropylcarbinyl tosylate or cyclobutyl β-naphthalenesulfonate and **3**-ONas is due to changing medium effect. These results are consistent with the response of **3**-ONas solvolysis rate to medium effects relative to that of cholesteryl tosylate.[9]

A plot of the solvolysis rates of crotyl β-naphthalenesulfonate, an isomer of **3**-ONas, against those of cholesteryl tosylate is used as an additional test of the above solvent relationship and is shown in Figure 1. It can be seen that the data are well correlated for all solvents with the exception of ethanol. If the value of $k_{EtOH}/k_{90\%\ dioxane}$ for crotyl β-naphthalenesulfonate (8.1) were the same as that for **3**-ONas (2.3) or cholesteryl tosylate (2.5), the point for ethanolysis would fit on the correlation line. Although the interpretation of Figure 1 is somewhat complicated by the enhanced sensitivity of crotyl β-naphthalenesulfonate to nucleophilic assistance in ethanol, nevertheless the satisfactory correlation between two substrates with widely different structures but similar mode of charge dispersal in the transition state is accented by the failure of ei-

(1) D. D. Roberts, *J. Org. Chem.*, **34**, 285 (1969), and previous papers.
(2) D. D. Roberts, *ibid.*, **30**, 23 (1965).
(3) D. D. Roberts, *ibid.*, **31**, 2000 (1966).
(4) K. L. Servis and J. D. Roberts, *Tetrahedron Lett.*, 1369 (1967).
(5) C. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, **74**, 145 (1952).
(6) S. Borcic, M. Nikoletic, and D. E. Sunko, *ibid.*, **84**, 1615 (1962).
(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 86 ff.
(8) H. L. Goering, N. D. Nevitt, and E. F. Silversmith, *J. Amer. Chem. Soc.*, **77**, 5026 (1955).
(9) D. D. Roberts and T. M. Watson, *J. Org. Chem.*, **35**, 978 (1970).

TABLE I

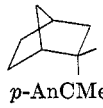
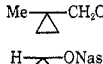
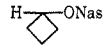
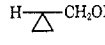
SUMMARY OF SOLVOLYSIS RATES FOR ORGANIC NASYLATES

Compd	Solvent	Temp, °C	k_1, 10^5 sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[b] eu
	AcOH	17	16.9	16.8 ± 0.1	−18 ± 1
	AcOH	18	19.4		
	AcOH	20	24		
	AcOH	22	30		
	AcOH	25	42		
	AcOH	30	64		
	AcOH	35	106		
	AcOH	38	132		
	AcOH	40	158		
	EtOH	20	6.2	21.4 ± 0.1	−5 ± 1
	EtOH	25	12		
	EtOH	30	21		
	EtOH	35	40		
	EtOH	40	69		
	AcOH	20	0.12	23.0 ± 0.1	−7 ± 1
	AcOH	30	0.42		
	AcOH	40	1.5		
	AcOH	50	5.0		
	AcOH	60	14.2		
	EtOH	40	0.53	22.4 ± 0.2	−12 ± 1
	EtOH	50	1.36		
	EtOH	65	7.7		
	EtOH	70	12.6		
Cholesteryl tosylate	AcOH	30	0.77	23.6 ± 0.1	−4 ± 1
	AcOH	50	10		
	AcOH	65	50		
Cholesteryl tosylate	EtOH	40[c]	3.4	24.8 ± 0.3	−1 ± 2
	EtOH	50[c]	10.0		
	EtOH	78[d]	300		
Crotyl nasylate	80% EtOH	40	0.31		
	85% EtOH	40	0.24		
	90% EtOH	40	0.13		
	EtOH	40	0.08		
	MeOH	40	0.17		
	80% dioxane	40	0.05		
	85% dioxane	40	0.03		
	90% dioxane	40	0.01		
	85% acetone	40	0.04		
	90% acetone	40	0.02		

[a] Uncertainties (one standard deviation from the mean). [b] Uncertainties (one standard deviation from the mean). [c] Taken from data of ref 9. [d] Taken from data of Stoll, *Z. Physiol. Chem.*, **246**, 6 (1937).

TABLE II

SUMMARY OF ACTIVATION PARAMETERS FOR SELECTED COMPOUNDS

Compd	AcOH $\Delta H^{\ddagger}$	AcOH $\Delta S^{\ddagger}$	EtOH $\Delta H^{\ddagger}$	EtOH $\Delta S^{\ddagger}$	Ref
 OBS	21.6	−7			*a*
p-AnCMe$_2$CH$_2$OTs	23.1	−5	23.6	−6	*b*
Chlolesteryl OTs	23.6	−4	24.8	−1	*c*
	23.0	−7	16.2	−16	*d*
	23.0	−7	22.4	−12	*c*
	16.8	−18	21.4	−5	*c*

[a] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1154 (1952). [b] S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956). [c] This work. [d] Reference 3.

ther Y values[10] or log k_{ion} values[11] to correlate with the crotyl β-naphthalenesulfonate rate data.

The experiments summarized in Table III were conducted to further study the ion-pair phenomena in the solvolysis reactions of **3**-ONas. Treatment of the salt data according to eq 1 yields a satisfactory correlation.

$$k_t = k_t^0 [1 + b\ (\text{salt})] \quad (1)$$

The high[12] b value for **3**-ONas acetolysis is in line with solvent sensitivity and is identical with that for *exo*-

(10) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).
(11) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).
(12) Values of b are typically 10–15 for primary sulfonates and 20–40 for secondary sulfonates: see S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

norbornyl brosylate and cyclobutyl β-naphthalenesulfonate acetolysis. For both these systems there is considerable support for anchimerically assisted solvolyses involving a homocyclopropenyl nonclassical ion.[13]

In acetic acid, the decrease in internal-return isomerization with increasing perchlorate concentration parallels the medium effect (for example cyclopropylcarbinyl chloride undergoes solvolysis in 80% aqueous, ethanol accompanied by 34% internal-return isomerization,[14] in 50% aqueous ethanol accompanied by 20% internal-return isomerization,[15] and in water unaccompanied by internal-return isomerization[16]) and implies that k_S/k_R increases with increasing perchlorate concentration. This is attributed to enhanced dissociation of intimate[17] ion pairs induced by the salt ion atmosphere.

The b value obtained for the ethanolysis of **3**-ONas supports a limiting type mechanism; however, in this solvent internal-return isomerization is invariant to salt concentration, *i.e.*, k_S/k_R remains constant with increasing perchlorate concentration. This result suggests that in ethanolysis of **3**-ONas, unlike solvolysis in acetic acid or 93% aqueous dioxane,[18] salt induced dissociation of intimate ion pairs is not competitive with solvent capture. It is also noteworthy that contrary to the solvolytic behavior of α,α-dimethylallyl chloride[19] in ethanol the intimate ion-pair intermediate generated from **3**-ONas is not completely diverted into solvolysis in the more nucleophilic solvent.

The product data recorded in Table IV show that, contrary to a previous report,[20] a similar product distribution is obtained for both the ethanolysis and acetolysis of cyclopropylcarbinyl arenesulfonates. It seems probable that a common cationic intermediate is captured by both solvents; however, the conclusions[21] that unimolecular rearrangements are occurring with frequencies in excess of solvent and ion-pair relaxations precludes the use of product distribution data for unambiguous assessment of charge dispersal in the transition state. This speculation is further supported by the finding[1] that the first formed cation generated in the solvolysis of 1-phenylcyclopropylcarbinyl tosylate differs significantly from that captured by the solvent.

Experimental Section

Melting points are uncorrected and were taken on a Mel-Temp apparatus. Infrared spectra were determined on a Shimadzu Model IR-27G spectrophotometer. A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector and 6 ft × 0.25 in. columns of 20% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W (30–60 mesh) and 20% sucrose acetate isobutyrate on Chromosorb W (30–60 mesh) was used for analytical gc work.

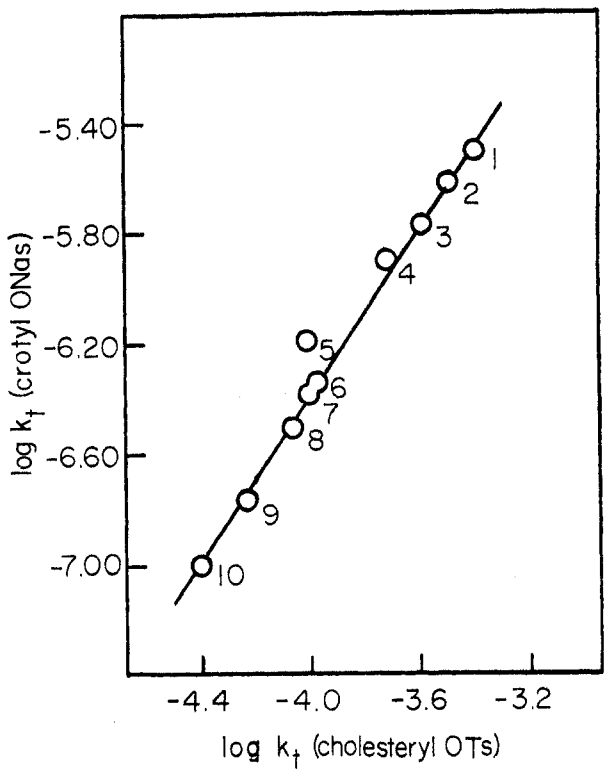


Figure 1.

Cyclopropylcarbinyl β-naphthalenesulfonate (**3**-ONas) was prepared in 50% yield according to established procedure,[18] mp [after three recrystallizations from 1:1 petroleum ether (bp 30–60°)-ether] 52–53° (lit.[18] mp 52–53°).

Cyclobutyl β-naphthalenesulfonate (**4**-ONas) was prepared in 55% yield as described for **3**-ONas, mp [after three recrystallizations from 1:1 petroleum ether (bp 30–60°)-ether] 75–76° (lit.[18] mp 75–76°).

Crotyl β-naphthalenesulfonate resulted when 2-naphthalenesulfonyl chloride (8.0 g, 0.35 mol) was mixed with crotyl alcohol (bp 122°, 2.16 g, 0.30 mol) and 35 ml of dry pyridine at 0°. After standing 24 hr at 0°, acidified reaction mixture with cold, 10% aqueous HCl. The separated oil was taken up in methylene chloride and dried (Na_2SO_4), and volatile components were removed by flash distillation under reduced pressure (0.1 mm) to yield an oil (2.0 g) of 99% purity by infinity titer: ir (neat) 1352 (SO_2 asym) and 1182 cm^{-1} (SO_2, sym). The sample was transparent in the 3600–3200-cm^{-1} region.

Cholesteryl tosylate was the same material as previously described.[9]

Solvents.—Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride. Acetone was purified by distillation from potassium permanganate. Absolute ethanol and dioxane were prepared according to the methods of Fieser.[22]

Cyclopropylcarbinyl Tosylate Ethanolysis Products.—Cyclopropylcarbinyl tosylate (95% purity, 5.6 g, *ca.* 25 mmol) was solvolyzed in 50 ml of ethanol (containing 50 mmol of pyridine) at 25° for ten half-lives. The material was dissolved in 40 ml of methylene chloride, washed first with cold dilute HCl, followed by several cold water washes, and dried (Na_2SO_4), and most of the solvent was removed by distillation. Analysis by gc revealed the presence of both ethyl cyclopropylcarbinyl ether and cyclobutyl ether.

Kinetic experiments were carried out as previously described.[2,23] The uncertainties for the rate constants varied from 0.2 to 1.0 standard deviation units from the mean. The temperature of the kinetic baths was maintained within a ±0.05° range.

(13) See P. H. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.
(14) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).
(15) K. L. Servis and J. D. Roberts, *Tetrahedron Lett.*, 1369 (1967).
(16) C. Y. Wu and R. E. Robertson, *ibid.*, **88**, 2666 (1966).
(17) External return is ruled out by the observation that lithium tosylate induces the normal salt acceleration effect.
(18) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *J. Amer. Chem. Soc.*, **83**, 4843 (1961).
(19) P. B. D. De La Mare and C. A. Vernon, *J. Chem. Soc.*, 2504 (1954).
(20) D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965); later glpc investigations revealed that a dioctyl phthalate column as well as Carbowax 20M and Apiezon grease columns failed to separate ethyl cyclopropylcarbinyl ether and ethyl cyclobutyl ether.
(21) P. S. Skell and R. J. Maxwell, *J. Amer. Chem. Soc.*, **84**, 3963 (1962).
(22) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 285.
(23) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

TABLE III

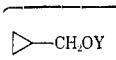
SUMMARY OF SOLVOLYSIS RATES IN THE PRESENCE OF SALTS

Arenesulfonate	[Ester] × 10^2	Salt	[Salt] × 10^2	k_1, 10^5 sec^{-1}	Infinity,[a] %	b value[b]
Cyclopropyl-carbinyl[c]	3.0			24	50	
	3.0	LiOAc	5.0	26	54	
	3.0	LiOAc	10.0	29	55	
	3.0	LiOTs	5.0	28	48	
	3.0	$LiClO_4$	0.1	25	50	38
	3.0	$LiClO_4$	0.5	30	54	
	3.0	$LiClO_4$	1.0	34	55	
	3.0	$LiClO_4$	3.0	53	57	
	3.0	$LiClO_4$	5.0	73	58	
	3.0	$LiClO_4$	10.0	124	63	
Cyclopropyl-carbinyl[d]	3.0			6.2	90	
	3.0	Urea	5.0		90	
	3.0	$LiClO_4$	0.1	6.3	90	7
	3.0	$LiClO_4$	0.5	6.5	90	
	3.0	$LiClO_4$	1.0	6.6	90	
	3.0	$LiClO_4$	3.0	7.3	90	
	3.0	$LiClO_4$	5.0	8.3	90	
	3.0	$LiClO_4$	10.0	10.5	90	
Cyclobutyl[e]	3.0			5.0	91	
	3.0	$LiClO_4$	1.0	6.8	91	38
	3.0	$LiClO_4$	5.0	14.5	92	
	3.0	$LiClO_4$	10.0	24	94	
Cyclobutyl[f]	3.0			1.36	100	
	3.0	$LiClO_4$	3.0	1.7	100	7
	3.0	$LiClO_4$	10.0	2.4	100	
Cholesteryl[g]						28
Cholesteryl[h]	1.0			9.2		
	1.0	$LiClO_4$	3.0	10.5		4
	1.0	$LiClO_4$	10.0	13.3		

[a] Percentage of the theoretical acid liberated after eight half-lives. [b] Calculated from the equation $k_t = k_t^\circ [1 + b (salt)]$: A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763, 2767, 2777, 2780 (1956). [c] β-Naphthalenesulfonate in acetic acid at 20°. [d] β-Naphthalenesulfonate in ethanol at 20°. [e] β-Naphthalenesulfonate in acetic acid at 50°. [f] β-Naphthalenesulfonate in ethanol at 50°. [g] *p*-Toluenesulfonate in acetic acid at 50°: taken from data of S. Winstein and E. Clippenger, *J. Amer. Chem. Soc.*, **78**, 2784 (1956). [h] *p*-Toluenesulfonate in ethanol at 50°.

TABLE IV

SOLVOLYSIS PRODUCTS

Compd	Solvent-buffer	Y	Products: 		CH_2=CH-CH_2CH_2OY
3 tosylate[a]	AcOH–AcO$^-$	AcO	71	24	5
3 tosylate	EtOH–C_5H_5N	EtO	75[b]	25	Trace

[a] Data taken from ref 20. [b] Ethyl cyclopropylcarbinyl ether did not rearrange after ten half-lives in ethanol containing *p*-toluenesulfonic acid and pyridine buffer.

Registry No.—**3**-ONas, 26366-57-4; **4**-ONas, 26366-58-5; crotyl β-naphthalenesulfonate, 26366-59-6; cholesteryl tosylate, 26438-43-7; cyclopropylcarbinyl tosylate, 1015-45-8.

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