[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Hydrolysis of Sodium Alkyl Sulfates in Basic Aqueous Solution[1]

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RECEIVED MARCH 9, 1955

Hydrolysis of the following sodium alkyl sulfates in basic aqueous solution has been investigated at temperatures in the vicinity of 100 to 150°: methyl, ethyl, propyl, isobutyl, neopentyl, isopropyl, *s*-butyl 1-ethylpropyl and pinacolyl. In the sequence methyl to isobutyl two types of hydrolysis occur, one independent of, and one proportional to hydroxide ion concentration. The ratio k_2/k_1 declines from 60 to 5.3 in this sequence. For the other compounds, second-order hydrolysis is relatively small (isopropyl and *sec*-butyl) or undetectable (neopentyl and pinacolyl). The second-order reaction is a typical nucleophilic displacement reaction. The first-order reaction seems to be transitional between S_N1 and S_N2. Both types of hydrolysis exhibit a positive salt effect. Neopentyl and pinacolyl involve substantially complete rearrangement during hydrolysis; isobutyl involves partial rearrangement. However, 1-ethylpropyl hydrolyses without rearrangement and optically active *sec*-butyl hydrolyses with inversion of configuration and with very little racemization. Accordingly, in the simple sodium alkyl sulfates, some degree of covalent binding of water seems to occur in the transition state. For ethyl and propyl, hydrolysis is unaccompanied by detectable olefin formation. With isobutyl, a small percentage of the reaction leads to isobutylene. Isopropyl apparently involves both first- and second-order olefin formation. With pinacolyl, slightly more than a third of the product is olefin.

In basic aqueous solution, the hydrolysis of sodium ethyl sulfate and of sodium methyl sulfate is reported to be second order.[3,4] The hydrolysis of sodium (+)*sec*-butyl sulfate under similar conditions is first order, yet it proceeds with inversion of configuration and with very little racemization.[5]

It appeared of interest to study such hydrolyses in greater detail, particularly since they involve the departure of an ion (the sulfate ion) of twice the charge of the departing ions in the examples of hydrolysis most extensively studied (alkyl halides and *p*-toluenesulfonates). This augmented charge separation might be expected to introduce features of mechanistic interest. We report here the examination of the hydrolyses in basic aqueous solution of nine sodium alkyl sulfates.

Owing to a relatively much more rapid acid-catalyzed hydrolysis,[5] it was necessary to work in solutions with enough initial caustic to keep them basic throughout a run.

Experimental

Materials.—Sodium methyl, ethyl and isopropyl sulfates were prepared by mixing slowly and with cooling roughly equal numbers of moles of the alcohol and 95% sulfuric acid. These mixtures were allowed to stand for two days. The other sodium alkyl sulfates were prepared by reaction of alcohols with sulfamic acid and pyridine.[6] Each reaction mixture was neutralized with concd. sodium hydroxide solution and evaporated to dryness at room temperatures. The sodium alkyl sulfate was separated from the sodium sulfate or sodium sulfamate by extraction with methanol. The filtrate from this step was evaporated to dryness at room temperature and the process repeated. In the sulfamic acid–pyridine preparation, the evaporating solutions were kept at *p*H 12 to facilitate the elimination of ammonia since, otherwise, difficultly removable ammonium alkyl sulfates contaminate the product. The final methanolic solution was acidified with sulfuric acid to decompose carbonate, exactly neutralized, filtered and evaporated. The resulting material was recrystallized from methanol–isopropyl alcohol mixtures except for sodium neopentyl and sodium pinacolyl sulfates which were too soluble. Isopropyl alcohol alone was used for the first and 9:1 petroleum hexane and isopropyl alcohol, for the second. In preparations, yield was sacrificed to purity. Under such conditions yields of sodium alkyl sulfates *via* the sulfamic acid process were about 50%.

The salts were analyzed by ignition to sodium sulfate[6] with the results shown in Table I.

TABLE I

ANALYSES OF SODIUM ALKYL SULFATES

Alkyl group	Sodium sulfate, %	Alkyl group	Sodium sulfate, %
Methyl	99.9	Neopentyl	98.7
Ethyl	100.4	*sec*-Butyl	100.2
Isopropyl	99.9	1-Methylbutyl	100.4
Propyl	99.8	1-Ethylpropyl	99.5
Isobutyl	99.4	Pinacolyl	100.5

Kinetic Procedures.—In a kinetic run, seven to nine identical 10-cc. units of aqueous solutions of a sodium alkyl sulfate and sodium hydroxide free of carbonate were prepared. The concentrations of the two reactants were approximately equal unless otherwise stated. The units were introduced into a thermostat, removed in sequence and rapidly cooled. They were analyzed by acidimetry using calibrated apparatus and using methyl orange as the indicator. At the lowest concentration of reactants (0.002 *M*), potentiometric titration was necessary. Acidimetry measures the summed extents of both substitution and elimination.

$$C_nH_{2n+1}SO_4^- + OH^- = C_nH_{2n+1}OH + SO_4^{--} \quad (1)$$

$$C_nH_{2n+1}SO_4^- + OH^- = C_nH_{2n} + H_2O + SO_4^{--} \quad (2)$$

Conversions were ordinarily carried to 60 to 70%.

Mr. Lars Hellberg investigated the basic hydrolysis of sodium isopropyl sulfate in Pyrex glass tubes at 99°. His results agreed with those described below, but his data possessed more scatter owing to the lack of a satisfactory method of correcting for release of alkali from the glass.[7]

In this research, reactors were made from Monel tubing 1.8 cm. in diameter and 8.1 cm. long. The lower end of the tubing was closed by silver-soldering a Monel disk across the end. In runs at 99°, the other end was closed with a rubber stopper pierced by a capillary tube. After the reactors had been at 99° for a few minutes, they were sealed by means of a screw clamp on a piece of rubber tubing attached to the outside end of the capillary. At the higher temperatures, pressures above atmospheric were developed. The reactors were then closed by a miniature Ipatieff closure, in which a copper gasket is pressed between knife edges by means of six Allen-head bolts. The parts involving the knife edges were of stainless steel. Joining was by silver-soldering. These autoclaves were weighed before and after a run. No instance of leakage was detected.

The reactors and rubber stoppers were conditioned by heating for several days with 0.5 *M* sodium hydroxide solution. After this conditioning the titer of sodium hydroxide solutions would be unchanged after several days heating in the reactors at 99°.

Concentrations of reactants were established at 25°. One could probably adequately correct for the effects on concentration of the expansion of the solutions by using

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[1] Presented at 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

[2] To whom queries about this paper should be addressed.

[3] G. A. Linhart, *Am. J. Sci.*, **185**, 283 (1913).

[4] G. H. Green and J. Kenyon, *J. Chem. Soc.*, 1389 (1950).

[5] R. L. Burwell, Jr., THIS JOURNAL, **74**, 1462 (1952).

[6] R. L. Burwell, Jr., *ibid.*, **71**, 1769 (1949).

[7] L. Hellberg, Senior Thesis, Northwestern University, 1951.

TABLE II

RATE CONSTANTS[a] IN THE HYDROLYSIS OF SODIUM ALKYL SULFATES IN ALKALINE AQUEOUS SOLUTION

Run	C_0[b]	T, °C.	Order	$k_1' \times 10^6$	$k_2' \times 10^6$	$k_1 \times 10^6$	$k_2 \times 10^6$
Sodium methyl sulfate (I)							
Ia	0.001986	138.3	1	8.53		7.92	
Ib[c]	.01006	138.0	1 + 2			7.73	464
Ic	.2505	79.6	2		12.16		
Id	.2519	98.9	2		68.8		64.5
Ie	.2523	109.0	2		182.6		
If	.5025	98.7	2		81.6		78.9
Ref. 4	.5	100.0	2		83		
Sodium ethyl sulfate (II)							
IIa	0.002022	138.5	1	5.25		5.10	
IIb	.00995	110.2	1	0.676			
IIc	.00995	138.0	1	4.85		4.30	
IId	.01022	150.5	1	9.80			
IIe[c]	.05002	138.0	1 + 2			4.58	91.6
IIf	.2511	98.9	2		7.11		5.93
IIg	.2509	138.0	2		143.5		120
IIh	.5013	98.9	2		7.93		7.21
Ref. 4	1.0	100.0	2		10.5		
Sodium propyl sulfate (III)							
IIIa	0.00998	138.1	1	3.06		2.79	
IIIb	.4999	99.1	2		3.14		2.77
Sodium isobutyl sulfate (IV)							
IVa	0.01002	138.3	1	0.704		0.681	
IVb	.00990	151.5	1	1.930			
IVc[d]	.5021	99.0	2 + 1		(0.236)		0.153
IVd	.5029	138.3	2 + 1		(7.30)	.934	4.85
Sodium neopentyl sulfate (V)							
Va	0.5026	138.8	1	0.416		0.416	<0.08
Vb	.5005 .1016[e] .133[f]	138.1	1	.381		.381	
Vc	.5043	164.0	1	3.58		3.58	<0.7
Sodium isopropyl sulfate (VI)							
VIa	0.01006	98.9	1	2.71		2.70	
VIb	.02494	98.9	1	2.82		2.78	
VIc	.04992	98.9	1	2.92		2.84	
VId	.05013	109.4	1	7.06			
VIe	.04988	138.0	1	69.0			
VIf	.1004	98.9	1	3.07		2.92	
VIg[c]	.2497	98.9	1 + 2			3.13	
VIh[c]	.5010	98.9	1 + 2			3.40	2.7
VIi	.05059 .1333[f]	98.9	1	3.36		3.28	
VIj	.0502 .400[g]	98.9	1	3.51		3.43	
VIk	.1012 .0503[e]	98.9	1	2.92		2.85	
VIl	.1005 .2003[e]	98.9	1	3.45		3.04	
VIm	.1017 .0333[f]	98.9	1	3.18		3.04	
VIn	.0993 .0991[g]	98.9	1	3.28		3.12	
Sodium *sec*-butyl sulfate (VII)							
VIIa	0.01005	98.9	1	3.58		3.57	
VIIb	.05070	98.9	1	4.25		4.20	
VIIc[c]	.5025	98.9	1 + 2			5.35	2.1

TABLE II (*Continued*)

Run	C_0[b]	T, °C.	Order	$k_1' \times 10^6$	$k_2' \times 10^6$	$k_1 \times 10^6$	$k_2 \times 10^6$
			Sodium pinacolyl sulfate (VIII)				
VIIIa	0.01005	99.1	1	5.69		5.69	
VIIIb	.01005	108.9	1	12.61		12.61	
VIIIc	.5027	98.9	1	6.66		6.66	
			Sodium 1-ethylpropyl sulfate (IX)				
IXa	0.00996	99.3	1	6.42			

[a] Units of rate constants are concentrations in moles per liter at 25° and time in seconds. k_1' and k_2' are the apparent rate constants derived from conventional plots in those cases in which reasonably close approach to straight-line behavior was observed. k_1 and k_2 are constants derived in cases of parallel first- and second-order reactions (see text) or are the apparent rate constants corrected for relatively small amounts of contribution of the other order (see text). [b] Concentration of the sodium alkyl sulfate unless otherwise indicated. The concentration of sodium hydroxide was nearly the same unless otherwise indicated. [c] Rate constants were derived from treatment of reaction as parallel first- and second-order reactions. [d] k_2 is from initial rate corrected for first-order contribution. The reaction was carried to but 20% conversion which required nearly 40,000 minutes. [e] Concentration of NaOH. [f] Concentration of Na_2SO_4. [g] Concentration of $NaClO_4$.

the relative expansion of pure water. The relative volumes of water are 25°, 1.003; 100°, 1.044; 130°, 1.070 and 160°, 1.102.[8] One could readily compute the second order rate constants in terms of concentrations corrected from 25°. However, on this basis, one would make no correction for those reactions which we have found to be first order; yet water is here clearly involved in the molecularity. In view of this difficulty, of the probable change of activity coefficients with temperature and of the change of the nature of the medium with temperature, the rate constants are computed from the concentrations in moles per liter at 25° without corrections. Corrections would not affect the matter of primary interest in our kinetic data, which is the ratios of the values of the rate constants for the various sodium alkyl sulfates.

Thermostating was by vapor-baths. Since runs were often protracted to several days, variation of barometric pressure entailed some variation in temperature. The observed time intervals were corrected *via* the observed activation energies to conform to a constant mean temperature. Such corrections were commonly less than 2%.

Where possible, rate constants were found by conventional first- and second-order plots using the best straight line.[9] Rate constants so evaluated are listed as k_1' (first order) and k_2' (second order) in Table II. Concentration units are moles per liter and time units, seconds. The original rate data are available in the Ph. D. thesis of George M. Calhoun, Northwestern University, 1954.

In most cases, plots were straight lines to within the scatter of the data. In certain cases, however, curved lines were obtained with both first- and second-order plots. The reactions appeared to be parallel first- and second-order reactions. In such a reaction of mixed order[10]

$$\ln\left[\frac{C_0}{(k_1/k_2) + B_0}\right]\left[\frac{(k_1/k_2) + B_0 - X}{C_0 - X}\right] = k_2t[(k_1/k_2) + B_0 - C_0] \quad (3)$$

Here, C_0 and B_0 are the initial concentrations of sodium alkyl sulfate and of sodium hydroxide. Values of the function on the left side of equation 3 divided by t were computed for various ratios of k_1/k_2. That ratio which gave the closest approach to constancy throughout the run was chosen as correct. Such values of k_1 and k_2 are listed in Table II. This procedure does not result in highly precise values of rate constants. The probable error in the ratio seemed to be about ±10%. Where a reaction of one order dominates, the rate constant of that reaction is relatively precise whereas that of the other is particularly lacking in precision.

The ratios of initial *rates* of first- and second-order reactions were: run Ib, 1.7; IIe, 1.0; IVd, 0.4; VIh, 2.4; VIIc, 5.4. No second-order contribution could be detected in the reactions of sodium neopentyl and pinacolyl sulfates at 0.5 *M*; that is, k_2/k_1 is less than about 0.2.

Although reasonably good first- and second-order plots were obtained in most runs, the relative values of k_1 and k_2 indicate that there must have been some contributions of the reaction of the other order. Owing to the inevitable scatter of points, it is not easy to detect minor contributions of the reaction of other order. From the value of k_1/k_2, as determined, correction was made for this minor contribution.

For predominantly first-order reactions, k_1' was corrected by use of equation 3 in the form ($C_0 - B_0 = 0$)

$$k_1 = \frac{1}{t}\ln\left(\frac{C_0}{C_0 - X}\right) + \frac{1}{t}\ln\left(1 - \frac{k_2X}{k_1 + k_2B_0}\right)$$

By dividing by

$$k_1' = \frac{1}{t}\ln\left(\frac{C_0}{C_0 - X}\right)$$

one eliminates t. The slope of the first-order plots seemed to be predominantly determined by points in the vicinity of conversions of 60%. Setting $X = 0.6\ C_0$

$$k_1 = k_1'\left[1 + \frac{1}{\ln 2.5}\ln\left(1 - \frac{0.6\ C_0(k_2/k_1)}{1 + (k_2/k_1)B_0}\right)\right]$$

For predominantly second-order plots, points at lower conversions seemed more determining. Thus, approximately

$$k_2'C_0^2 = k_1C_0 + k_2C_0^2$$

and

$$k_2 = \frac{k_2'C_0}{(k_1/k_2) + C_0}$$

Corrected values of k_1' and k_2' (k_1 and k_2) are shown in Table II.

Table III shows experimental activation energies (E_a) and activation entropies[11] as determined by the summed rates of equations 1 and 2. The apparent rate constants, k_1' or k_2', were used since k_1 or k_2 were not available at different temperatures. The activation energies differ but little and this reduces the error from the use of k_1' and k_2'. The error from this cause is a maximum with both reactions of sodium ethyl sulfate and with the second-order reaction of sodium isobutyl sulfate. The second-order hydrolysis of sodium methyl sulfate and the first-order hydrolyses of sodium ethyl and sodium isopropyl sulfate were determined at three temperatures, the others at but two.

TABLE III

ACTIVATION ENERGIES AND ENTROPIES OF ACTIVATION

Group	Order	Molarity	Temp. range, °C.	E_a, kcal.	$\Delta S^‡$, e.u.
Methyl (I)	2	0.25	80–109	24.0	−15.7
Ethyl (II)	1	.01	110–150	22.2	−39.8
	2	.25	99–138	23.4	−22.2
Isobutyl (IV)	1	.01	138–151	26.6	−32.7
	2	.5	99–138	26.8	−22.1
Neopentyl (V)	1	.5	138–164	26.2	−35.0
Isopropyl (VI)	1	.05	99–138	24.6	−28.3
Pinacolyl (VIII)	1	.01	99–109	23.0	−31.7

In computing the entropies of activation for the first-order reactions, it was assumed that the reactions were ac-

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(8) N. E. Dorsey, "Properties of Ordinary Water-substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 583.

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 47.

(10) Reference 9, p. 152.

(11) Reference 9, Chapter 5.

tually second order, *i.e.*, first order in H_2O. The first-order rate constants were therefore divided by the concentration of water at 25°, 55.5 *M*.

Olefin Yield.—The yield of olefin in equation 2 was determined for most sodium alkyl sulfates. Where the olefin was gaseous, the reaction vessel was a 60-cc. Monel flask provided with a standard taper joint into which was fitted a vertical tube to serve as a reflux condenser. The end of this tube was connected *via* stopcocks to a gas buret and to an expansion chamber in both of which water was the containing fluid. The total empty volume of the system was 117.5 cc. In a determination, 50 cc. of a reaction mixture was refluxed very gently for a suitable period of time. Gas driven out of the reactor vessel and reflux condenser during warm-up and olefin evolved during reaction were taken into the expansion chamber. The apparatus was then cooled to room temperature and kept at least 12 hours during which time gas flowed back into the system from the expansion bulb. The water level in the expansion bulb was adjusted to its original volume and the excess gas read in the gas buret. Corrections were made for change in barometric pressure, ambient temperature and change in aqueous tension caused by the change in temperature. Good blanks were obtained with distilled water in the reactor but solubility of olefin in the final solution in the reactor vessel and in the water in the expansion bulb could not readily be corrected for. Because of this, the listed percentage olefin yields may be low by 10–15% of the listed olefin fraction. Following olefin measurement, the residual solution in the reactor was titrated to determine the total extent of reaction.

With sodium isopropyl sulfate, an attempt at a material balance was made by titrating the isopropyl alcohol by the method of Cassar[12] whenever olefin yields were determined.

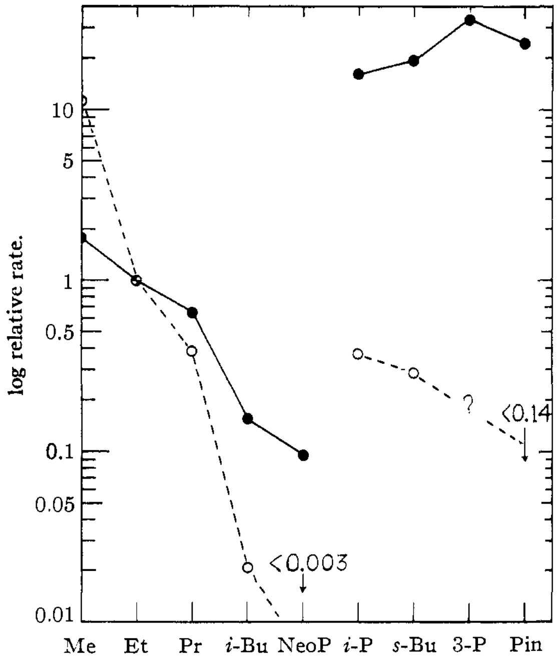

Fig. 1.—Values of k_1 (full line) and k_2 (dashed line) relative to ethyl. For k_1 the values are for 138.0° and for initial concentrations of sodium alkyl sulfate and sodium hydroxide equal 0.01 *M*. Observed activation energies were employed in correcting values to 138.0°. The activation energies for *sec*-butyl and 1-ethylpropyl were assumed equal that of isopropyl. The observed value of k_1 for neopentyl at 0.5 *M* was corrected to 0.01 *M* on the basis of the salt effect observed for pinacolyl. The values of k_2 apply at 98.9° and 0.5 *M*. The listed maximum values for k_2 for neopentyl and pinacolyl are derived from kinetic measurements. One can reduce each by a factor of 10 since the product alcohol is substantially completely rearranged.

With proper adjustment of acid strength, potassium dichromate quantitatively oxidizes isopropyl alcohol without affecting the unhydrolyzed sodium isopropyl sulfate. In running knowns, about 97% of the isopropyl alcohol could be accounted for. Considering the somewhat imprecise nature of the olefin yield experiments, reasonable material balances were obtained, although, particularly with the more dilute solutions at high conversions, the total products accounted for fell as low as 85%.

Alcohol Recovery Experiments.—Basic hydrolyses of sodium 1-ethylpropyl sulfate (1.0 *M*) and sodium pinacolyl sulfate (0.5 *M*) were run in the apparatus shown in Fig. 1 of ref. 5. The organic phase was separated into olefin and alcohol by distillation in a micro-column. The spectrum of the alcohol in the first case was identical with that of 3-pentanol from 4.5 to 14.5 μ. In the second case, the spectrum indicated the presence of less than 10% of pinacolyl alcohol. Although a sample of 2,3-dimethyl-2-butanol was not available for spectroscopic comparison, the bulk of the isolated alcohol was presumably this compound. The sample, unlike pinacolyl alcohol, reacted rapidly with concentrated hydrochloric acid. The melting points of the 3,5-dinitrobenzoate and of its α-naphthylamine adduct[13] were too high for any other tertiary hexyl alcohol but were 8–10° below recorded values for 2,3-dimethyl-2-butanol. The probable presence of small amounts of other alcohols is thus indicated.

Hydrolyses of sodium isobutyl sulfate (0.5 *M*) and of sodium neopentyl sulfate (0.5 *M*) were run in the miniature autoclaves used for kinetic runs. Alcohols, recovered from the products in the apparatus described in the preceding paragraph, were distilled in a micro-column. The first hydrolysis proceeded for 67 hr. at 150.9° with 90 cc. of solution and the second for 139 hr. at 164° with 70 cc.

Discussion

The Second-order Reaction.—Previous workers[3,4] reported that hydrolysis of sodium methyl and sodium ethyl sulfates proceeds as a second-order reaction in basic solutions, *i. e.*, with a rate proportional to $[OH^-][NaSO_4R]$. Only concentrations greater than 0.5 *M* were examined. Actually, the primary alkyl sulfate anion hydrolyzes by two processes, the previously reported second-order reaction and a first-order reaction (independent of $[OH^-]$). The trends of the rate constants for the two reactions for a series of primary alcohols are shown in Table II and in Fig. 1. In Fig. 1, the sequence beginning at the left, methyl, ethyl, propyl, isobutyl and neopentyl, is one in which, following the superprimary group methyl, the ethyl group is progressively substituted by methyl groups in the β-position.

With sodium methyl sulfate, k_2/k_1 is about 60. Thus, at concentrations of sodium hydroxide of 0.17 *M* and greater, the reaction is substantially second order; that is, the initial rate of the second-order reaction is at least ten times greater than that of the first-order reaction. Using similar standards, substantially pure first-order hydrolysis would obtain at concentrations of sodium hydroxide below 0.0017 *M*. The two rates are initially equal at 0.017 *M*.[14] Both rate constants decrease with increasing substitution but, as shown in Fig. 1, k_2 declines much more rapidly than k_1. Thus, the concentration at which the two rates are initially equal increases in the sequence of alkyl groups given above. For ethyl it is 0.05 *M* and for isobutyl, 0.19 *M*. Since no second-order contribution could be detected with neopentyl, from kinetics k_2/k_1 is less than 0.2. Since the product

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[12] H. A. Cassar, *Ind. Eng. Chem.*, **19**, 1061 (1927).

[13] P. Sutter, *Helv. Chim. Acta*, **21**, 1266 (1938).

[14] The two rates are equal at $C = k_1/k_2$.

TABLE IV

RELATIVE RATES OF FIRST-ORDER SOLVOLYSES

	Methyl	Ethyl	Propyl	*i*-Butyl	Neopentyl	*i*-Propyl	*s*-Butyl
$ROSO_3^-$ in H_2O, 138°	1.79	1.0	0.65	0.15	0.090	16	19.5
RBr in 50% C_2H_5OH, 95°[18,19]	2.03	1.0	.57	.080	.0064	1.4	
ROTs in HOAc, 75°[18]	1.11	1.0		.31	.11	51	
$RO_3SC_6H_5$ in 56% acetone, 50°[20]	2.32	1.0	.56			9.7	14.2
Same in 17.8% acetone[20]		1.0				33	
Same in 50% dioxane, 50°[21]	2.01	1.0				15	
$RONO_2$ in 60% C_2H_5OH, 60°[22]	1.8	1.0				4.4	

At least partial SN1 character usually has been assumed to obtain in these apparently related reactions. If one were to use the ratio k_1(isopropyl)/k_1(ethyl) as a measure of the amount of SN1 character, the bisulfate esters would have somewhat less such character than the benzenesulfonic acid esters, since the data for solvolyses of the latter in 56 and 17.8% acetone[20] indicate that the ratio in water would be about 40 as compared with a ratio in water of 16 for bisulfate esters. This is plausible since benzenesulfonic acid is a stronger acid than the bisulfate ion, HSO_4^-.

of hydrolysis is *t*-amyl alcohol devoid of neopentyl alcohol, k_2/k_1 is actually probably less than 0.02.

The effect of substitution upon k_2 resembles that in a number of bimolecular nucleophilic displacement reactions[15,16] and the values of k_2 exhibit a positive salt effect appropriate to the charge type. The values of k_2 are small not only because of the activation energies but also because of the large negative entropies of activation (Table III) which are typical of reactions between ions of like charge.[17]

The computed second-order rate constants for sodium isopropyl and sodium *s*-butyl sulfates are nearly as large as that for sodium propyl sulfate. However, since with the secondary alkyl compounds, the second-order reaction accompanies a much faster first-order reaction, precision in k_2 is low. Furthermore, much of the second-order reaction may be an elimination reaction rather than a displacement. Any bimolecular substitution reaction of sodium secondary alkyl sulfates would be better studied in solvents more favorable to such reactions or with nucleophilic displacing species more active than the hydroxyl ion.

In acidic solution, hydrolysis of the alkyl sulfate anion is relatively fast and predominantly involves nucleophilic displacement on sulfur[5]

$$H_2O + HO_3SOR \longrightarrow H_2SO_4 + HOR$$

The R–O bond is not cleaved. This reaction is known to hydrolyze the neopentyl sulfate anion without rearrangement of the neopentyl skeleton. The observed rate of hydrolysis of sodium neopentyl sulfate in basic solution coupled with absence of neopentyl alcohol in the product indicates that the corresponding displacement on sulfur in the anion, proceeds a millionth as rapidly as the

$$H_2O + {}^-O_3SOR \longrightarrow HSO_4^- + HOR$$

analogous reaction with the alkylsulfuric acid. The negative charge on the anion would, of course, decrease the rate of nucleophilic displacement on sulfur. It would also decrease that of displacement on carbon (diethyl sulfate is a much more active alkylating agent than the ethyl sulfate anion) but to a lesser degree since the sulfur is more closely associated with the added negative charge.

The First-order Reaction.—The variation of k_1 with structure (see Fig. 1) somewhat resembles that of alkyl bromides in aqueous ethanol or aqueous dioxane[18,19] but, of reported reactions, it more closely resembles that of the solvolysis of alkyl sulfonate esters[18,20,21] and possibly alkyl nitrates.[22] Relative rates of these reactions are shown in Table IV.

Mere determination of rates in one solvent constitutes an inadequate base for the determination of mechanism. In the present study we apply the additional data provided by the stereochemistry of hydrolysis of optically active sodium *sec*-butyl sulfate, by the degree of rearrangement observed in alcoholic products and by the salt effect. It would be valuable to add a study of the kinetics in solvents of varying ratios of ionizing character to nucleophilic character.[23] The solubility characteristics of sodium alkyl sulfates would permit study in ethanol and in acetic acid.

The alcohol formed in the hydrolysis of sodium neopentyl sulfate at 164° was exclusively *t*-amyl. That from the hydrolysis of sodium isobutyl sulfate run at 151° to a computed conversion of 75% was 87% isobutyl and 13% *t*-butyl alcohol. From k_1/k_2, the fraction of the sulfate hydrolyzing by the first-order process was 40%. Thus, about one-third of the first-order reaction resulted in rearranged alcohol.

In the primary alcohol sequence, the transition state appears to contain contributions both from the conventional forms for nucleophilic displacement, $H_2O\ C\text{–}OSO_3^-$ and $H_2O^+\text{–}C\ OSO_3^{--}$, and from that for the carbonium ion process, $H_2O\ C\text{–}OSO_3^{--}$ and $H_2O\ C^+\ OSO_3^{--}$.[23] Contributions of the latter set would vary from little for methyl to predominant for neopentyl. A similar treatment could be given in terms of a molecular orbital theory.[24]

The hydrolyses of the unbranched *sec*-alkyl sodium sulfates present a somewhat unusual combination of features: near absence of racemization in the hydrolysis of optically active *sec*-butyl; lack of rearrangement in that of 1-ethylpropyl; yet dominant first-order hydrolysis and k_1(isopropyl)/k_1(ethyl) = 16. However, for an extreme type of

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[15] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 154.

[16] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Sections 23 and 29.

[17] Reference 9, pp. 139 and 132.

[18] S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952), Table V.

[19] I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 164 (1946).

[20] E. Tommila and J. Jutila, *Acta Chem. Scand.*, **6**, 844 (1952).

[21] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

[22] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1208 (1952).

[23] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

[24] W. von E. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953).

SN1 process (or **Lim.** in Winstein's terminology[23]), k_1 (isopropyl)/k_1(ethyl) should be at least 10^4.[23]

These factors suggest that the transition state for the secondary compounds involves enough of the character of a nucleophilic substitution to depress the augmentation of rate and to stabilize the structure against racemization and isomerization. In particular, a kinetically free carbonium ion seems absent. Although one might contend that such a species would react with solvent so rapidly that isomerization and racemization would be excluded, reaction involving a kinetically free carbonium ion should result in a much larger ratio, k_1(isopropyl)/k_1(ethyl), than actually observed. Thus significant binding of water must accompany the departure of the sulfate ion. It might be supposed that this would in part result from the large charge separation which would occur in a carbonium ion, C^+ SO_4^{--}. However, our conclusions as to mechanism are rather similar to those of Winstein[23] regarding the solvolysis of isopropyl tosylate.

We suggest that the degree of isomerization of 1-ethylpropyl is a criterion of the degree of approach to an extreme SN1 mechanism. In extreme types of SN1 reactions, the following reaction

$$\mathrm{C{-}\overset{+}{C}{-}C{-}C{-}C \rightleftarrows C{-}C{-}\overset{+}{C}{-}C{-}C}$$

approaches equilibrium since Friedel–Crafts alkylations[25,26] and transalkylation reactions[27] result in substantially equilibrium mixtures of 2- and 3-phenylpentane. Isomerization with but partial approach to equilibrium results from the action of such reagents as anhydrous hydrogen bromide on 2- or 3-pentanol.[28] In hydrolysis in basic solution of sodium 1-ethylpropyl sulfate, the 3-pentanol product contains less than 2% 2-pentanol as tested by infrared absorption.

It is doubtful whether the solvolysis of isopropyl benzenesulfonate should be classified as SN1[21] rather than transitional in the absence of examination of the degree of rearrangement of the *sec*-amyl analogs. In fact, reaction at reflux of the heterogeneous mixture of water and 1-ethylpropyl *p*-toluenesulfonate yields 3-pentanol containing no detectable quantity of 2-pentanol.[29] In water, the hydrolysis of sulfonate esters seems rather similar to that of the bisulfate esters. In acetic acid, however, *sec*-butyl tosylate yields *sec*-butyl alcohol which is 9% rearranged as determined by isotopic-carbon labeling.[30] Acetic acid as a solvent is well known to be particularly favorable to SN1 reactions. Much less rearrangement occurred in 25% water–75% acetone.

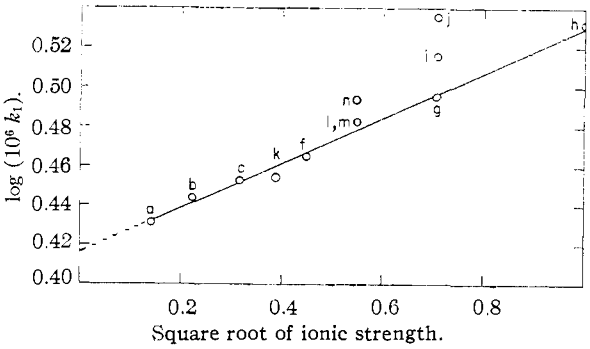
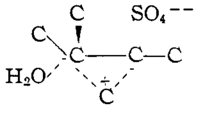


Fig. 2.—The salt effect in the first-order hydrolysis of sodium isopropyl sulfate at 98.9°. The letters on the graph refer to runs in section VI of Table II.

We suggest that the degree of rearrangement will be related to the degree of racemization in *sec*-butyl compounds and to other criteria[23] for the degree of approach to extreme SN1 reactions. Racemization of the *sec*-butyl group may, in part, occur consequent to rearrangement from the 2- to the 3-position.[26] Hydrolysis in basic solution of optically active sodium *sec*-butyl sulfate has been reported to yield an alcohol of inverted configuration and of an optical purity of at least 95%.[5] A repetition of run 3, Table I,[5] but with fractionation of the recovered alcohol gave an alcohol whose optical purity was 95%. Such small degrees of racemization are far below those customarily ascribed to SN1 reactions.[31,32]

Hydrolyses of sodium neopentyl and sodium pinacolyl sulfates are accompanied by substantially complete rearrangement, yet the rate of the latter is about the same as that of the unbranched *sec*-alkyl analogs which must have a different transition state. Similar near identity in k_1 has been observed for the equivalent esters of substituted benzenesulfonic acids.[33] The coincidence in the value of k_1 for pinacolyl with those of the other *sec*-alkyl bisulfate esters seem fortuitous since there is significant binding of water in the transition states of the unbranched *sec*-alkyl compounds and yet such binding at the carbon atom from which sulfate departs is very difficult with pinacolyl, conceptually because of steric hindrance and experimentally because of the drastic degree of rearrangement. Migration of a methyl group may contribute to the driving force of the solvolysis of pinacolyl either with[34] or without some degree of covalent binding of water to the site of its eventual attachment.



Salt Effect.—Positive salt effects occur with both k_1 and k_2. The simultaneous occurrence of first- and second-order reactions prevents accurate measurement of the salt effect in some cases. We examined the salt effect with sodium isopropyl sulfate at 98.9° in some detail as shown in Fig. 2.

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[25] H. Pines, W. D. Huntsman and V. N. Ipatieff, This Journal, **73**, 4483 (1951).

[26] R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

[27] R. L. Burwell, Jr., and A. D. Shields, *ibid.*, **77**, 2766 (1955).

[28] H. Pines, A. Rudin and V. N. Ipatieff, *ibid.*, **74**, 4063 (1952).

[29] Private communication from F. G. Bordwell and W. A. Hewett.

[30] J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., This Journal, **74**, 4283 (1952).

[31] Reference 16, p. 386.

[32] In the absence of values of k_1 for the various sodium alkyl sulfates given in this paper, we previously proposed that the hydrolysis of sodium *sec*-butyl sulfate must be SN2 to account for the lack of racemization (ref. 5). See also ref. 9, p. 242.

[33] Reference 18, Table IV. This paper contains an extensive discussion of the various factors which might influence such rates.

[34] C. G. Swain, This Journal, **70**, 1126 (1948).

The corrections for second-order contribution applied in converting k_1' to k_1 are of low precision but error in them will not affect conclusions.

The increased charge separation in the transition state of a mixed SN1–SN2 reaction should result in a positive salt effect[35] as observed. Sodium perchlorate (points j and n) and, to a lesser extent, sodium sulfate (i and m) exhibit specific salt effects in that they augment rates more than do the reactants. Sulfate ion exhibits no repressing common ion effect. The retarding effect of hydroxide ion reported to be general for unimolecular solvolyses[35a] does not appear in the hydrolysis of sodium isopropyl sulfate (point l).

In proceeding to completion, reactions 1 and 2 increase the ionic strength 50%. The consequent increase of k_1 with conversion during any one run is a small effect which is opposed by the contribution of the second-order reaction. We have ignored it.

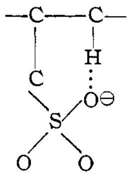
Olefin Formation.—The second-order hydrolysis of sodium ethyl (0.25 *M*) and sodium propyl (1.45 *M*) sulfates were unaccompanied by detectable olefin formation. The fraction of the hydrolysis of 2.0 *M* sodium isobutyl sulfate leading to olefin was about 0.04 but since no study was made of the effect of hydroxide ion concentration it is not known whether the olefin formation is first or second order.

At 1.0 *M*,[36] the olefin fraction from sodium 1-ethylpropyl sulfate was 0.21. At the same concentration, that from the pinacolyl was 0.37. There was no detectable second-order contribution to the reaction. With sodium *sec*-butyl sulfate at 0.25 *M*, the olefin fraction dropped from 0.31 at 17% conversion to 0.26 at 79%.

The olefin fraction from sodium isopropyl sulfate was investigated in greater detail. At low concentrations, the fraction is 0.05 to 0.07 and seems to arise from a first-order process. The fraction increases with increasing concentrations at a rate which appears too large for a salt effect. Probably, olefin formation occurs by both first- and second-order processes but our data are not precise enough to warrant much mathematical analysis. At 2.0 *M*, the olefin fraction was 0.24 at 16 to 56% conversion; at 0.5 *M* and similar conversions it was 0.15. At 0.1 *M* at conversions of 30, 57 and 69%, the olefin fractions were 0.11, 0.10 and 0.08. At 0.05 *M* and a conversion of 70%, the fraction was 0.07.

A few olefins were examined by infrared absorption spectroscopy. The butylene evolved from a refluxing solution of 0.25 *M* sodium *sec*-butyl sulfate carried to 45% conversion consisted of *cis*-2-butene, 44%; *trans*-2-butene, 39%; and 1-butene, 17% (all ±3%). The pentene from 1.0 *M* sodium 1-ethylpropyl sulfate was roughly an equimolecular mixture of *cis*- and *trans*-2-pentene. There was little or no *t*-butylethylene (the unrearranged olefin) in the product from sodium pinacolyl sulfate.

First-order elimination reactions have often been assumed to be associated with SN1 reactions. However, it is also possible that unimolecular formation of olefin can occur by a mechanism like that for ester pyrolysis.[37,38] A similar formation of olefin may occur in acid solutions from the alkylsulfuric acid.[5] In any case, solid barium *s*-butyl sulfate decomposes to butylene at about 100°[39] by a mechanism which must closely resemble that of ester pyrolysis.



Acknowledgment.—The authors express their thanks to the Research Corporation for the support of this research.

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(35) (a) Reference 9, pp. 138–142; (b) ref. 16, section 27.

(36) As in other cases, $[OH^-] = [RSO_4Na]$.

(37) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

(38) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(39) R. L. Burwell, Jr., THIS JOURNAL, **67**, 220 (1945).