HYDROLYSIS OF A SERIES OF PRIMARY ALKYL CHLOROSULFATES ENTROPY OF ACTIVATION AS A CRITERION OF FRAGMENTATION IN SOLVOLYTIC REACTIONS^{1,2}

E. BUNCEL AND J. P. MILLINGTON

Department of Chemistry, Queen's University, Kingston, Ontario Received October 13, 1964

ABSTRACT

The solvolysis of the series of alkyl chlorosulfates, $ROSO_2Cl$, where R = methyl, ethyl, *n*-propyl, isobutyl, and neopentyl, has been studied in 10 *M* aqueous dioxane. The relative reactivities fit well a solvolytic mechanism involving displacement by water on carbon, with OSO₂Cl as the leaving group. The change in mechanism of solvolysis from bimolecular with the straight-chain chlorosulfates to unimolecular with neopentyl chlorosulfate is shown by the absence of the lyate ion effect and the observation of rearrangement in the latter case.

The entropies of activation in chlorosulfate solvolysis appear to be abnormally large. It is proposed that the abnormal ΔS^{\pm} indicates a transition state in which both carbon-oxygen and sulfur-chlorine bond weakening occurs. It is shown that some other solvolytic reactions that are characterized by abnormally high entropies of activation may be interpreted on the basis of multiple bond fission (fragmentation). The mechanism of S_Ni reactions is considered in this context.

The preceding paper (1) considered in detail the reaction of a typical primary alkyl chlorosulfate with nucleophiles. Here we report the results of a solvolytic study on the series of primary alkyl chlorosulfates $ROSO_2Cl$, where R is methyl, ethyl, *n*-propyl, isobutyl, and neopentyl.

The products of reaction of dilute solutions $(0.01 \ M)$ of the alkyl chlorosulfates in 10 M aqueous dioxane were determined (Table V, Experimental section). The ionic products are H₂SO₄ and HCl, formed in quantitative yield. The major organic product in each case was the alcohol, with a trace of olefin as side product. The major reaction is therefore that represented by eq. [1], i.e. a simple hydrolysis, the olefin being formed most probably by a minor competing elimination reaction. In the case of neopentyl chlorosulfate, the alcohol formed is that from rearrangement, viz. *t*-pentyl alcohol.

[1]

$ROSO_2Cl + 2H_2O \rightarrow ROH + H_2SO_4 + HCl.$

The kinetic data were measured in 10 M aqueous dioxane, 85.3% dioxane – 14.7% water, by weight. The concentration of chlorosulfate employed was 0.01 M. Rates were measured conductimetrically. The half-lives of the hydrolyses were found to vary from the order of a minute in the case of the methyl compound to several hours for the neopentyl. The pseudo-first-order rate constants were calculated from usual plots which were linear over at least 75% of reaction and usually over 90% of reaction. Results for hydrolysis at several temperatures are given in Table I. Rate constants when calculated for each point individually within a run agreed to $\pm 1\%$ (standard deviation). The reproducibility between runs was generally also $\pm 1\%$. The rate constants given in Table I are the values from two separate runs. E_a and log A were obtained from a least-square plot. The error in E_a is estimated as ± 0.35 kcal/mole, and in ΔS^{\ddagger} , ± 1.0 entropy units (e.u.).

The Bimolecular and the Unimolecular Mechanism

One of the criteria used in evaluating the mechanism of solvolysis is the lyate ion

¹Part II in series of solvolysis of alkyl chlorosulfates. Part I, preceding paper.

²Presented in part at the 47th Annual Conference of the Chemical Institute of Canada, Kingston, Ontario, June 1964.

Canadian Journal of Chemistry. Volume 43 (1965)

BUNCEL AND MILLINGTON: HYDROLYSIS OF PRIMARY ALKYL CIILOROSULFATES

$k imes 10^4$ (s ⁻¹)					7			
ROSO₂Cl	9.94 °C	14.95 °C	19.95 °C	24.97 °C	34.99 °C	45.01 °C	E_{a} (kcal)	$\log A$ (s ⁻¹)
Methyl	$\begin{array}{c} 57.0\\ 56.7\end{array}$	$\frac{82.3}{83.2}$	143 143	$\frac{210}{210}$			14.4	8.85
Ethyl	$rac{21.7}{22.5}$	33.5 33.1	$\frac{48.9}{48.5}$	72.2 71.2			13.2	7.54
<i>n</i> -Propyl	10.5 10.6	17.5 17.5	$27.6 \\ 27.6$	$39.5 \\ 40.1$			14.2	7.97
Isobutyl				3.10 3.08	$8.90 \\ 9.05$	$\frac{21.8}{22.1}$	18.2	9.83
Neopentyl				$\begin{array}{c} 0.167 \\ 0.169 \end{array}$	$\begin{array}{c} 0.640 \\ 0.650 \end{array}$	$egin{array}{c} 2.22 \\ 2.21 \end{array}$	24.6	13.24

TABLE I
Hydrolysis of chlorosulfates (0.01 M) in 10 M aqueous dioxane

effect (2). The large lyate ion effect with *n*-propyl chlorosulfate $(k_{\rm OH}-/k_{\rm H_{2O}} = 380 \pm 30)$ was strongly indicative of a bimolecular mechanism of solvolysis. Since a change in mechanism along the series might be anticipated, it was of interest to determine how the lyate ion effect might vary. The rate of hydrolysis of neopentyl chlorosulfate was totally unaffected by base. The absence of a lyate ion effect in this case is indicative of a unimolecular carbonium ion mechanism (2). This is confirmed by the observation of rearrangement; *t*-pentyl alcohol was the only product formed, apart from a trace of olefin, in solvolysis of neopentyl chlorosulfate.

The relative reactivities of the series of alkyl chlorosulfates studied is informative. The results, relative to ethyl chlorosulfate as standard, are shown in Table II which also gives the results of some other nucleophilic substitutions of primary compounds containing displaceable groups. The reactions are arranged in a decreasing order of magnitude of the rate ratio of methyl (or ethyl) to neopentyl.

Reactions 1 and 6 represent two extremes in the effect of environment on reactivity. In reaction 1, which is a bimolecular displacement reaction, steric hindrance plays a dominant role and is responsible for the extremely low relative reactivity of the neopentyl compound. In reaction 6, solvolysis of the neopentyl compound actually proceeds at a faster rate than that of the methyl, so that clearly steric hindrance has now no importance; a limiting mechanism is indicated, that is a unimolecular carbonium ion mechanism with no participation by nucleophile in the transition state. However, even in formolysis some nucleophilic participation in the transition state must occur, since optically active 1-deutero primary systems react with inversion (3). In solvolysis of neopentyl derivatives there is no evidence for nucleophilic participation, but whether or not a migrating methyl group participates in the rate-determining transition state has not been settled (4, 5). An excellent discussion of this topic has been given (6).

The hydrolysis of alkyl chlorosulfates appears between the solvolysis of alkyl p-toluenesulfonates in pure ethanol and the solvolysis of alkyl bromides in 50% aqueous ethanol, in the reactivity order of Table II. Now solvolysis in ethanol (reaction 2) is considered (6) to be closely similar to the bimolecular displacement with ethoxide ion (reaction 1), so that in ethanolysis participation by the solvent molecule in the transition state must be very extensive (with the exception of the neopentyl case). By analogy, in the hydrolysis of alkyl chlorosulfates in 85.3% aqueous dioxane, solvent must likewise play an important role in the rate-determining transition state. Thus the above constitutes strong evidence in support of our view that alkyl chlorosulfates react with water in aqueous dioxane by

557

CANADIAN JOURNAL OF CHEMISTRY. VOL. 43, 1965

TUDDE H	Т	[A]	ΒL	Ē	IΙ
---------	---	-----	----	---	----

Reaction	CH_3	CH ₃ CH ₂	CH ₃ CH ₂ CH ₂	(CH ₃) ₂ CHCH ₂	(CH ₃) ₃ CCH ₂	Ref.
1. RBr + EtO [−] in EtOH, 55° 2. ROTs, EtOH, 75° 3. ROSO₂Cl, 85.3% aq. dioxane,* 25°	$17.6 \\ 2.3 \\ 2.93$	$1.0 \\ 1.0 \\ 1.0 \\ 1.0$	0.281	$\begin{array}{c} 0.0297 \\ 0.046 \\ 0.0431 \end{array}$	$\begin{array}{c} 0.00000423\\ 0.00057\\ 0.00235\end{array}$	7 4 This
4. RBr, 50% aq. EtOH,† 95° 5. RBr, 70% aq. EtOH,† Ag+, 64° 6. ROTs, HCOOH, 75°	$1.94 \\ 0.81 \\ 0.56$	$\begin{array}{c}1.0\\1.0\\1.0\end{array}$		$\begin{array}{c} 0.075 \\ 0.085 \\ 1.22 \end{array}$	$\begin{array}{c} 0.00625 \\ 0.013 \\ 1.0 \end{array}$	5 5 4

	1.10101		
Relative rate of	substitution of	some primary	compounds

*Expressed as weight %. On a volume % basis this would be 82%. †Expressed as volume %.

bimolecular displacement on carbon, with the exception of neopentyl chlorosulfate which reacts by a unimolecular carbonium ion mechanism.

It is also noteworthy that the sequence of reactions 2–6, obtained by arranging these in the order of decreasing magnitude of the rate ratio methyl:neopentyl, also represents the order of increasing ionizing power of the medium, and the chlorosulfate hydrolysis fits exactly into this sequence on both accounts. This gives added weight to the above argument.

Activation Parameters

In the series ethyl, *n*-propyl, isobutyl, neopentyl, there is a steady change in both ΔH^{\pm} and ΔS^{\pm} , the former increasing in magnitude and the latter becoming more positive (Table III). A plot of ΔH^{\pm} against ΔS^{\pm} is shown in Fig. 1. The slope of the straight line drawn through the points representing the above compounds, but excluding methyl, is 443.4 °K, which is the isokinetic temperature. Since the isokinetic temperature has a value far above the temperature of the experimental, interpretation of the data is free from the uncertainties arising when the isokinetic temperature is close to the experimental range (8). The enthalpy-entropy compensation effect observed in this reaction series is paralleled by the behavior of many other solvolytic reactions, for instance the solvolysis in water of alkyl methanesulfonates and bromides (9a). For one member of the series to deviate from this relationship is also not uncommon and in the present could be caused by the greatly reduced steric requirements of the transition state of the methyl case. It is also noteworthy that the neopentyl case falls on the isokinetic line with the alkyl chlorosulfates, methanesulfonates, and bromides (9a), even though neopentyl derivatives hydrolyze with rearrangement. Thus neopentyl derivatives seem to provide an exception to the general rule that a change in mechanism along a reaction series should be reflected by a deviation from the isokinetic relationship.

Entropy of Activation as a Criterion of Fragmentation

Further insight into the mechanism of chlorosulfate solvolysis is gained by consideration of the actual magnitudes of the activation parameters. A discussion of activation parameters must consider their dependence on the medium and on the mechanism of reaction. Thus the entropy of activation of solvolytic reactions conducted in aqueous organic solvents becomes rapidly more negative as the water content of the medium decreases (10) and a unimolecular mechanism is in general associated with a more positive entropy of activation, by 20 or more e.u., than a bimolecular reaction (11). The last point is well illustrated in the present series; ΔS^{\ddagger} for neopentyl chlorosulfate is 20-26 e.u. more positive than for the straight-chain chlorosulfates.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

558



FIG. 1. Plot of ΔH^{\ddagger} vs. ΔS^{\ddagger} for solvolysis of chlorosulfates.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

Comparison of the rates and activation parameters in chlorosulfate solvolysis with other solvolytic reactions, in the same reaction medium (Table III), shows at first glance that chlorosulfates react considerably faster and that in general lower enthalpies and greater entropies of activation are responsible for this enhanced reactivity. For a more searching comparison heed must be taken that two compared substrates should solvolyze by the same mechanism. It then becomes apparent that chlorosulfate solvolysis is associated with a more positive ΔS^{\ddagger} , by 10–15 e.u. Considering first unimolecular solvolysis, t-butyl chloride, t-butyl bromide, α -phenylethyl chloride, α -phenylethyl bromide, and benzhydryl chloride all solvolyze with ΔS^{\pm} varying between -11 and -15 e.u., while ΔH^{\pm} varies between 20 and 22 kcal (12). Similarly, isopropyl benzenesulfonate, with ΔS^{\pm} = -13.3 e.u. and $\Delta H^{\ddagger} = 22.0$ kcal, reacts by the unimolecular mechanism (13). No data have been found for neopentyl derivatives in this medium. For a comparison with activation parameters in bimolecular solvolysis, fewer data are available in the literature covering the present reaction medium. The solvolysis of a number of sulfonyl chlorides (14) provides comparable data: a typical example is ethane sulforty chloride, with ΔS^{\pm} = -37.4 e.u. and $\Delta H^{\pm} = 12.8$ kcal. It appears then that in unimolecular as well as in bimolecular solvolysis, when ΔH^{\pm} is comparable (EtOSO₂Cl vs. EtSO₂Cl) or when the reverse order obtains (neoPeOSO₂Cl vs. t-BuCl), chlorosulfates react with a more positive ΔS^{\pm} . While this relationship has not been rigorously established, particularly in view of the many factors which can influence entropies of activation (9, 11, 12), yet it seems to be sufficiently well documented to warrant consideration of its possible mechanistic significance.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965

	$k \times 10^{4}_{(s^{-1})}(25^{\circ})$	ΔH^{*} (kcal)	$\Delta S^{\mp} (25^{\circ})$ (e.u.)	$\frac{\Delta F^{\pm} (25^{\circ})}{(\text{kcal})}$	Ref.
CH ₃ OSO ₂ Cl C ₂ H ₅ OSO ₂ Cl -C ₃ H ₇ OSO ₂ Cl -C ₄ H ₇ OSO ₂ Cl teo-C ₅ H ₁ OSO ₂ Cl C ₂ H ₅ SO ₂ Cl -C ₅ H ₇ OSO ₂ C ₆ H ₅ (CH ₃) ₃ CCl C ₆ H ₅ CH(CH ₃)Cl	$\begin{array}{c} 211 \\ 71.6 \\ 39.8 \\ 3.09 \\ 0.168 \\ 0.13 \\ 0.11 \\ 0.0025 \\ 0.010 \\ 0.0030 \end{array}$	$\begin{array}{c} 13.8\\ 12.6\\ 13.6\\ 17.6\\ 24.0\\ 15.3\\ 12.8\\ 22.4\\ 21.9\\ 22.0\end{array}$	$\begin{array}{r} -20.0 \\ -26.0 \\ -24.0 \\ -15.5 \\ 0.1 \\ -29.8 \\ -37.4 \\ -14.6 \\ -12.7 \\ -14.7 \end{array}$	$19.7 \\ 20.4 \\ 20.7 \\ 22.2 \\ 24.0 \\ 24.2 \\ 26.7 \\ 25.7 \\ 26.3 \\ $	This work 14 14 13 12a 12b

	TABLE III				
Rates and activation	parameters for solvolysis	in 1	0 M	aqueous	dioxane

The relative reactivities, the lyate ion effect and the effect of added nucleophiles (1) in chlorosulfate solvolvsis are entirely consistent with a normal solvolvtic mechanism. which can be unimolecular or bimolecular, with the leaving group being -OSO₂Cl. On this basis, the transition state, for the unimolecular mechanism, would be as shown in eq. [2]. For comparison, the transition state of solvolysis of alkyl benzene sulfonates is shown in eq. [3], which is chosen due to the similarity of the two structures.

0

[2]

[3]

[4]

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

0

One would predict a slightly greater charge separation in the chlorosulfate than in the arenesulfonate on account of the electronegative chlorine, though this could be to some extent counteracted by the conjugating ability of the aryl group in the sulfonate. On the whole then, the polarities of the two ground states are rather similar and the same would be expected for the two transition states. Since the differential solvation of initial and transition states is generally accepted (10) as the major factor governing entropies of activation, one would expect both reactions to have similar ΔS^{\pm} values, which is not the case.

Another transition state may be considered for chlorosulfate solvolysis, one in which carbon-oxygen as well as sulfur-chlorine bond weakening occurs (eq. [4]):

 $\begin{array}{ccc} & & O \\ \parallel & & \parallel \\ R - O - S - Cl \rightarrow R - O - S - - Cl \rightarrow R^+ + SO_3 + Cl^-. \\ \parallel & & \parallel \\ O \end{array}$

In this transition state there is a greater charge separation and also an incipient sulfur trioxide molecule is forming, to a degree which depends on progress along the reaction coordinate. Both these factors should give rise to an increased solvation of the transition state, and consequently a more negative ΔS^{\pm} compared with the situation in eq. [2]. However, the simultaneous fission of two bonds with formation of three fragments would

BUNCEL AND MILLINGTON: HYDROLYSIS OF PRIMARY ALKYL CHLOROSULFATES

561

result in an increased ΔS^{\ddagger} due to the gain of translational, rotational, and vibrational degrees of freedom. The balance of the two effects, a smaller ΔS^{\ddagger} due to solvation and a larger ΔS^{\ddagger} due to dissociation, is difficult to estimate a priori. Gas-phase reactions provide a parallel: abnormally high entropies of activation, by 10–20 e.u., are believed to be due to simultaneous rupture of two bonds (15). The fragmentation process in chlorosulfate solvolysis may, therefore, well result in an abnormally large entropy of activation. On this basis the transition state in chlorosulfate solvolysis may be represented by the following resonance structures:



Analogous structures may be written for the bimolecular mechanism. The importance of structures II and III is indicated by the reported (16) relative inertness of alkyl fluoro-sulfates.³ That I and II are contributing structures is further suggested by the fact that there are only very few examples of simple secondary chlorosulfate in the literature and that a tertiary chlorosulfate has never been reported.

Application to Other Systems

The hypothesis of the fragmentation process in chlorosulfate solvolysis is germane to the problem of the possible generality of multiple bond fission. The classical $S_{\rm N}i$ reaction provides an example of this possibility. For instance, the decomposition of alkyl chlorosulfites and chloroformates to alkyl halides may in theory proceed by alkyl-oxygen fission, by acyl-chlorine fission, or by both modes simultaneously. There is considerable evidence that in inert solvents these processes have a predominantly carbonium ion character (alkyl-oxygen fission) (17), and that in the gas phase a cyclic four-centered, possibly polar, transition state obtains (18). The entropies of activation of these processes appear to be normal, generally ranging between -10 and -20 e.u. A recent study (19) of another $S_{\rm N}i$ reaction, the decomposition of aralkyl thiocarbonates ROCOSR' to RSR' and CO₂, has provided evidence for simultaneous fission of the alkyl-oxygen and acyl-sulfur bonds, through the observation of specific electronic effects of R and R' on the rate of reaction. No entropies of activation were reported for the reaction.

The solvolysis of alkyl chloroformates in formic acid appears to be associated with an unusually high ΔS^{\pm} : ethyl and isopropyl chloroformates have ΔS^{\pm} values of -1.8 and -0.4 e.u. respectively (20). In contrast formolysis of the corresponding arenesulfonates proceeds with more negative ΔS^{\pm} , by 5–15 e.u. (4). It is therefore noteworthy that in the solvolysis of alkyl chloroformates there is evidence of both alkyl-oxygen and acyl-chlorine bond fission (20, 21).

The solvolysis of γ -aminoalkyl halides (IV) yields products of substitution, elimination, cyclization, and fragmentation at the C_{β}—C_{γ} bond (22). The proposed mechanism (22) is rate-determining ionization of the C—X bond to give V, followed by fast product-forming steps.



³Work is in progress to establish; his point on a quantitative basis.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 43, 1965

The entropies of activation in 80% ethanol – 20% water, –1.2 e.u. for X = Cl, and 1.6 e.u. for X = Br are 4 e.u. greater than for the corresponding *t*-butyl halides (12*a*, 12*c*). Further, on substitution of the Me₂N group of IV (X = Cl) by Me₂CH, ΔS^{\pm} becomes again 5 e.u. smaller and only products from substitution and elimination are obtained. Now the Me₂N group does not play a role in the transition state by anchimerically assisting ionization of C—X, since there is no rate acceleration compared with the isopropyl analogue. If significance can be attached to a difference in ΔS^{\pm} of only 4–5 e.u., an explanation for the greater ΔS^{\pm} with IV is that in the transition state for solvolysis there is partial C_B—C_Y bond weakening (VI).

The hypothesis that entropies of activation may provide an indication of multiple bond fission in solution processes must be advanced with considerable caution, in view of the intricate nature of the activation process (23) and the many factors which can influence activation parameters. Further entropy data, for $S_N i$ and other solvolytic processes, are needed and corroboration by other criteria which afford a direct measure of the extent of bond weakening (e.g. isotope effects) is desirable before the validity of this hypothesis can be fully evaluated.

EXPERIMENTAL

The chlorosulfates were prepared by a modification of the method described by Binkley (24). Sulfuryl chloride (1 mole) was placed in a three-necked flask equipped with a gas inlet tube, a dropping funnel, and a drying tube. The flask was cooled in a bath of solid carbon dioxide and acetone and the solution agitated by means of a stream of dry nitrogen, which also removed most of the hydrogen chloride produced in the subsequent reaction. The anhydrous alcohol (1 mole) was then added by means of the dropping funnel, over a period of 1 h; in the neopentyl case the alcohol was dissolved in anhydrous ether before addition. At the end of this time the mixture was allowed to warm up to approximately 0 °C. The crude product was then washed three times with ice water, and dried over magnesium sulfate. The products were all purified by repeated fractional distillation under reduced pressure. The chlorosulfates were stable for prolonged periods at 0 °C but at room temperature they gradually decomposed.

The physical properties are shown in Table IV. The infrared spectrum of each compound showed the characteristic absorption bands in the region of 1 190 and 1 410 cm⁻¹ due to the --OSO₂Cl group (25); there was no hydroxyl absorption. The nuclear magnetic resonance spectrum of neopentyl chlorosulfate showed only two peaks, one at $\tau = 8.97$, of area 9 units corresponding to the methyl group and one at $\tau = 5.80$, of area 2 units corresponding to the methylene group. This proved that no rearrangement had occurred during the synthesis.

	ROSO ₂ Cl	Methyl	Ethyl	n-Propyl	Isobutyl	Neopentyl
Boiling point (°C/mm)	Found Lit. (24)	$\frac{40/14}{48/29}$	42/10 43/10	52/10 53/10	30/1	33/1
Density (25°)	Found Lit. (24)	1.483 1.48	$1.348 \\ 1.35$	1.281 1.28	1.218	1.173
Refractive index	Found Lit. (24)	$1.412/22^{\circ}$ $1.414/20^{\circ}$	$1.413/25^{\circ}$ $1.416/20^{\circ}$	$1.420/20^{\circ}$ $1.422/20^{\circ}$	$1.420/25^{\circ}$	$1.422/25^{\circ}$
Anal. S %	Found	,		2,	18.29, 18.56 18.55	16.78, 17.15
C1 %	Found Calcd.				20.0, 20.3 20.57	17.10 18.7, 18.7 19.04

TABLE IV Physical properties of the alkyl chlorosulfates

Product Analysis

Preparation of Chlorosulfates

This was carried out as previously (1), Table V. It was found (vapor-phase chromatography (v.p.c.)) that methyl, *n*-propyl, isobutyl, and neopentyl chlorosulfates yielded methyl, *n*-propyl, isobutyl, and *l*-pentyl alcohol, respectively. No *t*-butyl alcohol was detected in the hydrolysis of isobutyl chlorosulfate. Whether reaction of neopentyl chlorosulfate also yielded some unrearranged neopentyl alcohol could not be determined by v.p.c., since neopentyl alcohol had the same retention time as dioxane under the conditions

562

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

FABLE V

Products of the hydrolysis of chlorosulfates $(0.01 \ M)$ in 10 M aqueous dioxane

Chlorosulfate	H ₂ SO ₄ produced (Mole %)	HCl produced (Mole %)	Olefin produced (Mole %)
Methyl	96.8	99.5	
Ethyl	101.4	97.7	<u> </u>
n-Propyl	99.4	99.6	-
Isobutyl	99.4	98.3	
Neopentyl	98.8	98.3	4.5

used. To obtain information on this point a method of estimating a mixture of neopentyl and t-pentyl alcohol from their infrared spectra was developed.

The infrared spectrum of t-pentyl alcohol in dioxane showed a strong band at 940 cm⁻¹ while neopentyl alcohol under the same conditions showed strong absorption at 1 017 cm⁻¹. Infrared spectra of mixtures of these alcohols in varying ratios but with the same total concentration (0.02 M) gave a calibration curve of concentration against $\tilde{\gamma}_0$ absorbance for each alcohol. Three reaction mixtures were then analyzed in this way and showed a total recovery of 88%, 87%, and 90% respectively of *t*-pentyl alcohol and 0%neopentyl alcohol, with an error in estimation of $\pm 5\%$.

Measurement of Rates

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

The kinetic data were obtained by the conductivity method already described (1). The data for the lyate ion effect with neopentyl chlorosulfate are as follows:

$[ROSO_2Cl] \times 10^2$	$[NaOH] imes 10^2$	$k \times 10^4 \ (25 \ ^{\circ}\text{C})$
(M)	(M)	(s ⁻¹)
1.00	0.54	0.174
1.00	0.90	0.171
1.00	5.4	0.172
1.02	9.0	0.170
0.50	4.5	0.171
0.52	9.0	0.172

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. E. Robertson for a stimulating discussion and the National Research Council for a Studentship (to J. P. M.) and a grant.

REFERENCES

- 1. E. BUNCEL and J. P. MILLINGTON. Can. J. Chem. This issue.
- E. BUNCEL and J. P. MILLINGTON. Can. J. Chem. Inis issue.
 C. K. INGOLD. Structure and mechanism in organic chemistry. Bell and Sons, London. 1953. Chap. 7.
 A. STREITWIESER, JR. J. Am. Chem. Soc. 77, 1117 (1955).
 S. WINSTEIN and H. MARSHALL. J. Am. Chem. Soc. 74, 1120 (1952).
 I. DOSTROVSKY, E. D. HUGHES, and C. K. INGOLD. J. Chem. Soc. 173 (1946).
 A. STREITWIESER, JR. Solvolytic displacement reactions. McGraw-Hill, N.Y. 1962. pp. 73, 135.
 I. DOSTROVSKY and E. D. HUGHES. J. Chem. Soc. 157 (1946).
 F. BUNNET. In Rates and mechanisms of reactions and the Relief by S. L. Eriess, F. S. Lewis, and

 - B. J. F. BUNNETT. In Rates and mechanisms of reactions, part I. Edited by S. L. Friess, E. S. Lewis, and A. Weissberger. Interscience Publishers, N.Y. 1961, p. 177. O. EXNER. Nature, 201, 488 (1964).
 (a) R. E. ROBERTSON, R. L. HEPPOLETTE, and J. M. W. SCOTT. Can. J. Chem. 37, 803 (1959).
 (b) G. KHONSTAM. The transition state. Special Publication No. 16. The Chemical Society, Lo ndon.
 - 1962. p. 179.

- 1962. p. 179.
 10. A. A. FROST and R. G. PEARSON. Kinetics and mechanism. John Wiley, N.Y. 1961. Chap. 7.
 11. L. L. SCHALAGER and F. A. LONG. Advan. Phys. Org. Chem. 1, 1 (1963).
 12. (a) S. WINSTEIN and A. H. FAINBERG. J. Am. Chem. Soc. 79, 5937 (1957).
 (b) A. H. FAINBERG and S. WINSTEIN. J. Am. Chem. Soc. 79, 1597 (1957).
 (c) A. H. FAINBERG and S. WINSTEIN. J. Am. Chem. Soc. 79, 1602 (1957).
 (d) S. WINSTEIN, A. H. FAINBERG, and E. GRUNWALD. J. Am. Chem. Soc. 79, 4146 (1957).
 13. E. TOMMILA and E. MERIKALLIO. Suomen Kemistilehti B, 26, 79 (1953). E. TOMMILA. Acta Chem. Scand. 9, 975 (1955).
 14. R. FOON and A. N. HAMBI V. Australian I. Chem. 15, 668 (1962).
- 14. R. FOON and A. N. HAMBLY. Australian J. Chem. 15, 668 (1962). 15. B. G. GOWENLOCK. Quart. Rev. London, 14, 133 (1960). C. STEEL and K. J. LAIDLER. J. Chem. Phys. 34, 1827 (1961).
- 16. J. MEYER and G. SCHRAMM. Z. Anorg. Allgem. Chem. 206, 24 (1932).

563

564

Can. J. Chem. Downloaded from www.nrcresearchpress.com by UNIVERSITY OF NORTH TEXAS LIBRARY on 11/11/14 For personal use only.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 43, 1965

- C. E. BOOZER and E. S. LEWIS. J. Am. Chem. Soc. 76, 794 (1954). D. J. CRAM. J. Am. Chem. Soc. 75, 332 (1953). K. B. WIBERG and T. M. SHRYNE. J. Am. Chem. Soc. 77, 2774 (1955). A. STREIT-WIESER, J.R. and W. D. SCHAEFFER. J. Am. Chem. Soc. 79, 379 (1957). K. L. OLIVIER and W. G. YOUNG. J. Am. Chem. Soc. 81, 5813 (1959).
 E. S. LEWIS and W. C. HERNDON. J. Am. Chem. Soc. 83, 1961 (1961).
 J. L. KICE and R. A. BARTSCH. Tetrahedron Letters, No. 25, 1693 (1963).
 E. W. CRUNDEN and R. F. HUDSON. J. Chem. Soc. 1076 (1962).
 C. A. GROB and F. A. JENNY. Tetrahedron Letters, No. 23, 25 (1960). C. A. GROB, F. OSTERMAYER, and W. RAUDENBUSCH. Helv. Chim. Acta, 45, 1672 (1962).
 R. E. ROBERTSON. Can. J. Chem. 42, 1707 (1964).
 W. W. BINKLEY. J. Am. Chem. Soc. 60, 2810 (1938).
 E. A. ROBINSON. Can. J. Chem. 39, 247 (1961).