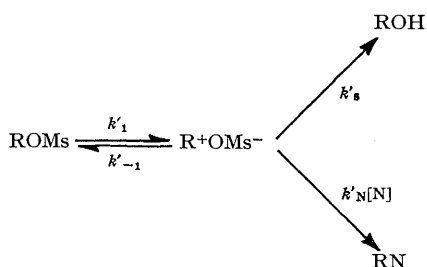


Evidence for Non-borderline Behaviour in the Reaction between 1-Methylheptyl Methanesulphonate and Sodium Azide in Aqueous Dioxan

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Rate constants and product proportions for the substitution reactions of 1-methylheptyl methanesulphonate (ROMs) in 25% dioxan-water containing varying amounts of sodium azide at constant ionic strength are reported. The first-order rate constants are linear with respect to $[\text{NaN}_3]$, as is the product ratio $[\text{RN}_3]:[\text{ROH}]$. If it is assumed that the rates of the competing azide-forming and solvolysis reactions are insensitive to changes in $[\text{NaN}_3]$ under conditions of ionic strength 'buffering', the rate-product correlation found is suggestive of identity of the rate-determining and product-determining steps. This is contrary to predictions based on the borderline variant of the Snee-Larsen 'unified' mechanism, which involves an intimate ion-pair as a common precursor of RN_3 and ROH . A suggestion that the concerted $\text{S}_{\text{N}}2$ mechanism may be mythical is thus seen to rest on unsure ground. A totally different situation prevails when diphenylmethyl chloride in 80% acetone-water is the substrate. The first-order rate constants are insensitive to changes in $[\text{NaN}_3]$ at constant ionic strength whilst the product-forming steps clearly involve competition between azide ion and water for an intermediate.

CENTRAL to the question of the mechanisms of nucleophilic substitution at a saturated carbon atom is the interpretation of kinetic and product results for the reactions between, for example, 1-methylheptyl methanesulphonate (ROMs) and azide ion and water in aqueous dioxan mixtures. Snee and Larsen¹⁻³ on one hand aver that the data are interpretable only in terms of nucleophilic attack occurring subsequent to the formation of a tight ion-pair (Scheme 1). Equations (1)–(3) apply to Scheme 1 ($[\text{N}] \gg [\text{ROMs}]$). In



SCHEME 1

these expressions, $x = k'_{-1}/k'_s$ and is assumed to be salt-independent, $m' = k'_N/k'_s$, and k_0 is the rate constant for solvolysis, which must be corrected in some empirical manner for salt effects when salt is present.^{1,2} As $x \rightarrow 0$, $k_{\text{obs}}/k_0 \rightarrow 1$, becoming independent of $[\text{N}]$, whilst as $x \rightarrow \infty$, $k_{\text{obs}}/k_0 = 1 + m'[\text{N}]$, i.e. the rate ratio becomes linearly dependent on $[\text{N}]$ and the slope is equal to the slope of the linear R vs. $[\text{N}]$ plot. The rate-product correlation is obtained because in this limit the rate-determining and product-determining steps (nucleophilic attack on the ion-pair) will be identical.

$$k_{\text{obs}} = \frac{k'_1(k'_s + k'_N[\text{N}])}{k'_{-1} + k'_s + k'_N[\text{N}]} \quad (1)$$

$$k_{\text{obs}}/k_0 = (1 + x)(1 + m'[\text{N}])/(1 + x + m'[\text{N}]) \quad (2)$$

$$R = [\text{RN}]/[\text{ROH}] = m'[\text{N}] \quad (3)$$

¹ R. A. Snee and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 362.

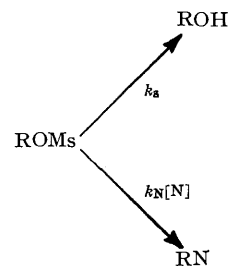
² R. A. Snee and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 6031.

³ R. A. Snee, *Accounts Chem. Res.*, 1973, **6**, 46.

⁴ R. A. Snee and W. A. Bradley, *J. Amer. Chem. Soc.*, 1972, **94**, 6975.

For intermediate values of x (say $0.5 < x < 10$)¹ equations (1) and (2) prevail, the plot of k_{obs}/k_0 vs. $[\text{N}]$ will be non-linear, and no direct rate-product correlation will be observed. Snee and his co-workers have claimed the demonstration of such a 'borderline' region for the reactions of not only ROMs with NaN_3 and water in dioxan-water mixtures,¹ but also for a variety of other reactions,²⁻⁶ and have been led to suggest that direct nucleophilic attack on covalent carbon as in the traditional $\text{S}_{\text{N}}2$ mechanism may be mythical. There is of course no doubt that ion-pairs are involved in a wide variety of nucleophilic substitution reactions,⁷ but the proposal that they may be necessary intermediates in *all* such processes is somewhat revolutionary.

On the other hand, Schleyer and his co-workers contend that the ROMs results can be interpreted in terms of competitive first-order and second-order reactions in which the rate-determining and product-determining steps are the same.⁸ This is shown in Scheme 2, which is in operational form only, with no



SCHEME 2

suppositions as to mechanism at this stage. From equations (4) and (5) pertinent to this process, it can be seen that a rate-product correlation exists. Among the mechanistic possibilities is the traditional $\text{S}_{\text{N}}1$ – $\text{S}_{\text{N}}2$

⁵ R. A. Snee and H. M. Robbins, *J. Amer. Chem. Soc.*, 1972, **94**, 7868.

⁶ R. A. Snee, G. R. Felt, and W. C. Dickason, *J. Amer. Chem. Soc.*, 1973, **95**, 638.

⁷ S. Winstein, B. Appel, R. Baker and A. Diaz, 'Organic Reaction Mechanisms,' *Chem. Soc. Spec. Publ.*, 1965, No. 19, p. 109.

⁸ D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4821.

dichotomy⁹ in which the second-order step involves attack by N on covalent carbon concerted with departure of the leaving group. No borderline region is permitted. Thus the survival of the S_N2 mechanism largely depends on the reality or otherwise of borderline kinetics.

$$k_{\text{obs}}/k_0 = 1 + k_{\text{N}}[\text{N}]/k_{\text{s}} \quad (4)$$

$$R = k_{\text{N}}[\text{N}]/k_{\text{s}} = m[\text{N}] \quad (5)$$

The markedly different interpretations placed by Sneen¹ and Schleyer⁸ on the same set of data arises from their differing assessment of the salt effect on k_0 . Sneen and Larsen¹ have used the salt effects of non-nucleophilic salts (LiClO₄, etc.) on the rate of solvolysis of ROMs as a model for the NaN₃ salt effect and in doing so have implicitly assumed that salt effects are both regular (k_0 linear with respect to [salt]) and almost non-specific (slope of k_0 vs. [salt] plots independent of the identity of the salt). Schleyer⁸ has employed the NaN₃ salt effect on k_0 as an adjustable parameter, and by assuming that k_0 decreases as [NaN₃] increases, has shown that the data are compatible with equations (4) and (5).

It is the purpose of the present work to reinvestigate the title reaction using conditions under which the salt effect on k_0 is hopefully minimized or eliminated, thus removing it as a source of ambiguity.

RESULTS AND DISCUSSION

The 1-Methylheptyl Methanesulphonate Reactions.— Kinetics and products of the decomposition of ROMs

[ROH] In each run was measured directly by g.l.c. analysis using an internal standard. However it proved impossible to obtain a satisfactorily constant g.l.c. molar response for RN₃ on the columns tried, and so [RN₃] was estimated titrimetrically in the usual way. This procedure has the advantage over the all-titrimetric methods previously employed^{1,4,5,10} in that any octenes formed are not counted as alcohol. In no case did %RN₃ + %ROH = 100, and the difference can be ascribed to minor products having the same g.l.c. retention times as a mixture of oct-1-ene and *cis*- and *trans*-oct-2-enes. Weiner and Sneen¹¹ have reported the formation of small quantities of olefins from the decomposition of 1-methylheptyl *p*-bromobenzenesulphonate in aqueous dioxan containing NaN₃. The outcome of the modified procedure was satisfactory in that values of $R/[\text{NaN}_3]$ [= m' in equation (3) and $k_{\text{N}}/k_{\text{s}}$ in equation (5)] were constant to within $\pm 2\%$, whereas a deviation of up to $\pm 15\%$ may be seen in the values derivable from titrimetric data alone.¹

Use of an excess of NaClO₄, the concentration of which decreases only by 15% as [NaN₃] is increased, may have two effects. First, the degree of dissociation of Na⁺N₃⁻ ion-pairs should remain invariant as [NaN₃] increases.^{12,13} However this is not important in the present context, as any salt effects on the k'_{N} or k_{N} terms are manifested in rate equations and product equations in the same way.⁴ Secondly, it was hoped that k_0 would remain constant as [NaN₃] was varied because of the constancy of the total salt concentration. This crucial assumption can be approached in two ways.

TABLE 1

The reactions of 1-methylheptyl methanesulphonate^a with azide ion and water in a 25% dioxan–water mixture at 35°

[NaN ₃]/M	[NaClO ₄]/M	10 ⁴ k_{obs}/s^{-1} ^b	RN ₃ (%) ^{b,c}	ROH(%) ^{b,c}	$R/[\text{NaN}_3]$ ^d	$k_{\text{N}}/k_{\text{s}}$ ^e
0	1.719	1.99 ± 0.07		99.1 ± 0.5		
0	1.864	2.15 ± 0.05		98.6 ± 0.6		
0	2.012	2.11 ± 0.06		98.8 ± 0.5		
0.0512	1.953	3.33 ± 0.05	38.2 ± 0.2	61.0 ± 0.4	12.2	11.3
0.0758	1.920	4.16 ± 0.07	48.1 ± 0.2	50.7 ± 0.5	12.5	12.8
0.0994	1.901	4.71 ± 0.07	53.1 ± 0.1	45.7 ± 0.4	11.7	12.5
0.153	1.852	5.89 ± 0.12	64.6 ± 0.4	34.0 ± 0.4	12.4	11.7
0.199	1.796	7.34 ± 0.20	69.7 ± 0.3	28.6 ± 0.4	12.2	12.5
0.253	1.749	8.23 ± 0.25	74.2 ± 0.3	24.9 ± 0.3	11.8	11.5
0.311	1.694	10.0 ± 0.3	77.5 ± 0.4	20.6 ± 0.2	12.1	12.0

^a [ROMs]₀ ca. 0.006M. ^b Uncertainties based on standard deviations. ^c Mean of three or more determinations. ^d Equal to m in equation (5), in l mol⁻¹. ^e From equation (4), in l mol⁻¹.

in 25% dioxan–water solvent containing various amounts of NaN₃ (0–0.3M) at constant total salt concentration (maintained at 2.0M by addition of NaClO₄) have been examined. First-order rate constants ($[\text{NaN}_3]_0 > [\text{ROMs}]_0$) and product proportions are shown in Table 1. A different procedure for determination of product ratios [RN₃]:[ROH] from that used by Sneen and his co-workers^{1,4,5,10} has been adopted.

⁹ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, 2nd edn., pp. 425–426.

¹⁰ R. A. Sneen and P. S. Kay, *J. Amer. Chem. Soc.*, 1972, **94**, 6983.

¹¹ H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 1965, **87**, 287.

¹² A. Fava, A. Iliceto, and A. Ceccon, *Tetrahedron Letters*, 1963, 685.

It is justified if we follow Sneen and assume that salt effects are both regular and non-specific. This may generally be the case, but some exceptions are known.¹⁴ Or, since NaClO₄ is present in excess (at least 5.6-fold) we may assume that it exerts the major component of the salt effect, and that the relatively small change in its concentration is kinetically insignificant. This is shown to be so by the first three entries in Table 1.

¹³ D. J. McLennan, *J.C.S. Perkin II*, 1972, 1577.

¹⁴ S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, 1960, 12; P. B. D. de la Mare, D. M. Hall, and E. Manger, *Rec. Trav. chim.*, 1968, **74**, 1394; J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, 1971, **36**, 897; C. L. Perrin and J. Pressing, *J. Amer. Chem. Soc.*, 1971, **93**, 5705; C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K. U. Yang, *J. Org. Chem.*, 1971, **36**, 887.

Thus the relatively small amount of NaN_3 present may exert only a minor salt effect at best as its concentration is varied, and the assumption is that this will not change k_0 by any large extent.

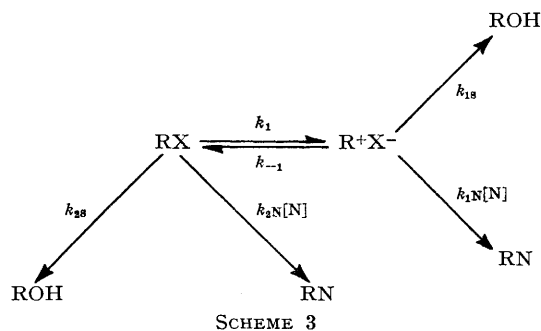
As can be seen from the last two columns of Table 1, the rate-product correlation required by equations (4) and (5) has been demonstrated. Calculation of relative rates by using the mean $R/[\text{NaN}_3]$ value from Table 1 in equation (4) in place of k_N/k_s gives excellent agreement with the measured relative rates as can be seen by comparing calculated ratios in column A of Table 2 with the experimental values.

TABLE 2
Comparison of measured k_{obs}/k_0 values with ratios calculated on the basis of various assumptions

[NaN_3]/M	k_{obs}/k_0 ^a	k_{obs}/k_0 (calc.)			
		A ^b	B ^c	C ^d	D ^e
0	1.00	1.00	1.00	1.00	1.00
0.0512	1.58 ± 0.16	1.62	1.37	1.58	1.34
0.0758	1.97 ± 0.20	1.92	1.50	1.87	1.55
0.0994	2.24 ± 0.22	2.20	1.61	2.12	1.65
0.153	2.79 ± 0.28	2.85	1.83	2.72	1.79
0.199	3.48 ± 0.35	3.41	1.98	3.20	2.03
0.253	3.90 ± 0.39	4.06	2.11	3.76	2.04
0.311	4.74 ± 0.47	4.76	2.24	4.34	2.24

^a Uncertainties calculated by conservatively assuming an error of ±5% in rate constants. This is considerably larger than observed standard deviations. ^b See text. ^c Calculated from equation (2) with $\alpha = 2.33$ and $m' = 12.0$. ^d Calculated from equation (2) using $\alpha = 40$ and $m' = 12.0$. ^e Calculated from equation (2) using $\alpha = 2.33$, $m' = 12.0$, and $10^4 k_0 = 2.11 (1 + 3.6[\text{NaN}_3])$.

On these grounds the borderline formulation may be rejected, within the framework of the salt effect assumption. A great many alternative mechanistic possibilities remain. $\text{S}_{\text{N}}2$ Attack of the nucleophiles N_3^- and water on ROMs is one obvious possibility (Scheme 3, with $k_{1s} = k_{1N} = 0$), the Snee-Larsen $\alpha \rightarrow \infty$ variant (Scheme 3, with $k_{2N} = k_{2s} = 0$ and



$k_{-1} + k_{1s} \gg k_{1N}[N]$) is another, and in a third, attack may occur at both covalent carbon and on an ion-pair (Scheme 3, with either $k_{-1} + k_{1s} \gg k_{1N}[N]$ or $k_{1N} = 0$). Other possibilities are more fully covered by Schleyer.⁸

Are our results in any way compatible with the borderline formulation? In column B of Table 2 are shown calculated values of k_{obs}/k_0 , obtained *via* equations (2) and (3) assuming $\alpha = 2.33$ (the value giving the best fit of the data of Snee and Larsen¹) and no salt effect

¹⁵ L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 979.

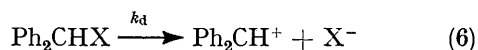
on k_0 . They do not agree with the experimental values. In fact, $\alpha = 40$ is needed to obtain agreement within experimental error, as shown by column C. However it is considered that such a high value of α takes the ion-pair mechanism out of the borderline region.¹

In Table 2 is shown an attempted correlation of the experimental rate ratios, adjusted empirically for a salt effect on k_0 (column D) with those calculated in column B from equation (2). It is seen that the present results are compatible with a borderline mechanism, but only if they are empirically adjusted so as to fit with ratios calculated by using a further adjustable parameter. This is scarcely satisfactory. The salt-assisted acceleration factor of 3.6 (Table 2, footnote *e*) is not outside the bounds of feasibility, but it does not accord with the values of *ca.* 1.0 found by Snee and Larsen for solvolysis of ROMs in the presence of non-nucleophilic salts. In any case, Snee has assumed that this factor is independent of the identity of the salt in his recent attempt to remove it from consideration as an adjustable parameter.^{4,5}

Therefore, no positive mechanistic conclusion can be reached. If the fundamental salt effect assumption is accepted however, doubt must be attached to the purported demonstration of borderline kinetics unique to ion-pair mechanisms. It then follows that firm experimental evidence against the concerted $\text{S}_{\text{N}}2$ mechanism has yet to be provided.

The Diphenylmethyl Chloride Reactions.—Interpretation of the ROMs results rests on the assumption that ionic strength ‘buffering’ ensures constancy of the first-order solvolytic component of the total rate. This is of course not directly experimentally verifiable, and an independent check is desirable.

The substitution reactions of diphenylmethyl halides in aqueous acetone have been shown to involve no nucleophilic participation in the rate-determining step. Bearing in mind the observation of common-ion retardation, the rate-determining step is as shown in equation (6), so that $k_{\text{obs}} = k_d$, the rate constant for dissociation in situations where common-ion retardation is unimportant.^{15,16} This in turn will be a function of some or all the rate constants pertaining to ionization of Ph_2CHX to an ion-pair-ion-pair interchange,¹⁷ and dissociation of the ion-pair. Thus



k_{obs} for Ph_2CHX is not exactly equivalent to k_0 for ROMs. However, NaN_3 affects both rate constants *via* salt effects alone. In 90% acetone-water, addition of 0.1M- NaN_3 increases the rate of destruction of $\text{Ph}_2\text{-CHCl}$ by a factor of 2.12, whilst there is an acceleration of 1.31-fold in 70% acetone-water. There is no rate-product correlation,¹⁵ and the rate-determining and product-determining steps are not identical.

¹⁶ Ref. 9, p. 468.

¹⁷ V. J. Shiner and R. D. Fisher, *J. Amer. Chem. Soc.* 1971, **93**, 2553.

We have already admitted the possibility that the k_0 route in the ROMs reaction could involve ionization, although it is not likely that dissociation also occurs, and in these terms, the salt effect on k_{obs} for Ph_2CHCl may serve as a reasonable model for the salt effect on ROMs solvolysis. Kohnstam and his co-workers¹⁸ have previously used the salt effect induced by NaN_3 on Ph_2CHCl decomposition rates as a model for the salt effect on the rate of hydrolysis of *p*-methoxybenzyl chloride in the presence of NaN_3 .

TABLE 3
The reactions of diphenylmethyl chloride with azide ion and water in 80% acetone-water

$[\text{NaN}_3]_0/[\text{M}]$	$[\text{NaClO}_4]_0/[\text{M}]$	$10^4 k_{\text{obs}}$ s^{-1} ^a	Ph_2CHN_3 (%) ^{a,b}	$R/[\text{NaN}_3]^{-1}$ l mol^{-1} ^c
0	0.998	5.31 ± 0.17		
0.0386 ^d	0.961	5.40 ± 0.12	13.8 ± 0.4	4.57 ± 0.22
0.0752	0.925	5.35 ± 0.14	23.2 ± 0.3	4.45 ± 0.09
0.103	0.901	5.39 ± 0.13	29.6 ± 0.3	4.40 ± 0.08

^a Uncertainties are standard deviations. ^b Mean of three or more determinations. ^c $[\text{NaN}_3]$ in denominator is mean of $[\text{N}_3^-]_0$ and $[\text{N}_3^-]_\infty$. HN_3 has been assumed to be a weak acid. A formally correct method of calculation is given by R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, 1966, **88**, 2594. ^d $[\text{Ph}_2\text{CHCl}]_0 = 0.00720\text{M}$ in this run. In all others, $[\text{Ph}_2\text{CHCl}]_0 = \text{ca. } 0.015\text{M}$.

In Table 3 we show first-order rate constants for the destruction of Ph_2CHCl in 80% acetone-water with the total salt concentration maintained at 1.0M by NaClO_4 . The addition of up to 0.1M- NaN_3 has a negligible effect on the rate constant under these conditions, an observation which may be contrasted with the aforementioned accelerations in 'unbuffered' media. A significant diversion of products to Ph_2CHN_3 is observed, and the ratio $R/[\text{NaN}_3]$ is effectively constant, indicating that the nucleophiles N_3^- and water compete for an intermediate or intermediates in fast steps occurring after the rate-determining step.

If it is accepted that k_{obs} for Ph_2CHCl in buffered media is an adequate model for k_0 in the ROMs reactions, our basic assumption of the previous section is justified.

The rate constant pattern for Ph_2CHCl in 'buffered' media is similar to that observed for 1-adamantyl bromide and 2-adamantyl toluene-*p*-sulphonate in unbuffered 80% ethanol-water containing sodium azide,⁸ and to the unbuffered methanolysis of di-(*p*-anisyl)methyl mesitoate in the presence of the same salt.¹⁹ The fact that NaN_3 causes no salt effect in these latter reactions, but does accelerate Ph_2CHCl decomposition, may merely be a consequence of the greater dielectric constants of the alcoholic solvents over those for 70–90% acetone-water.²⁰

EXPERIMENTAL

Materials.—1-Methylheptyl methanesulphonate, sodium azide, and dioxan were prepared and/or purified as described by Sneen and Larsen.¹ Diphenylmethyl chloride

¹⁸ G. Kohnstam, A. Queen, and B. Shillacker, *Proc. Chem. Soc.*, 1959, 157.

¹⁹ C. D. Ritchie, *J. Amer. Chem. Soc.*, 1971, **93**, 7324.

²⁰ Ref. 9, p. 485.

was prepared by the method of Ward.²¹ A mixture of oct-1-ene and *cis*- and *trans*-oct-2-enes was prepared by allowing 1-methylheptyl bromide (from the reaction between octan-2-ol, bromine, and triphenylphosphine in dimethylformamide) to react with sodium methoxide in methanol.²² The components of the mixture were not completely separated by g.l.c. (Varian Aerograph 1532-2B with flame ionization detector) on a 3 m QF-1 column at 35°. Methyl 1-methylheptyl ether, used as internal standard for g.l.c. analysis of octan-2-ol, was isolated after methanolysis of ROMs and was found to be octene-free (g.l.c.) after fractional distillation. Acetone was purified and dried by successive distillations from potassium permanganate and soda-lime. AnalaR sodium perchlorate monohydrate was used as received.

Kinetics.—Solvent mixtures were prepared by mixing 80 volumes of acetone with 20 volumes of degassed conductivity water or 25 volumes of freshly distilled dioxan with 75 volumes of water. (Sodium perchlorate was found to be insufficiently soluble in 30% dioxan-water mixtures containing NaN_3 for the present purposes.) Reaction mixtures were made up as described by Sneen and Larsen,¹ and the progress of the reactions, conducted under nitrogen, was followed by quenching 5 ml samples in cold acetone and titrating with standard sodium hydroxide using a Radiometer Titrigraph automatic titrator equipped with glass and calomel electrodes. At least three infinity samples were taken for each run (10–20 half-lives). Their titres (V_∞) were found to be constant and, in those runs

TABLE 4
Kinetics of the reaction between ROMs (0.006142M) with NaN_3 (0.0994M) in 25% dioxan-water containing NaClO_4 (1.901M) at 35°

Time/s	NaOH/ml ^a	$10^4 k_{\text{obs}}/\text{s}^{-1}$
0	0.143 ^b	
180	0.320 ^b	4.78
360	0.476 ^b	4.72
510	0.600 ^c	4.73
630	0.703 ^c	4.70
900	0.861 ^c	4.57
1040	0.983 ^c	4.65
1380	1.172 ^d	4.79
1975	1.427 ^d	4.68
2490	1.604 ^d	4.68
3530	1.865 ^d	4.78
10 Half-lives	2.264 ^{d,e}	
12 Half-lives	2.275 ^{d,e}	
15 Half-lives	2.273 ^{d,e}	

$$\text{Mean } k_{\text{obs}} = (4.71 \pm 0.07) \times 10^{-4} \text{ s}^{-1}$$

^a $[\text{NaOH}] = 0.00634\text{M}$. ^b Measured using 0.5 ml syringe burette. ^c Measured using 1.0 ml syringe burette. ^d Measured using 2.5 ml syringe burette. ^e Since V_∞ (theoretical) = 4.843 ml, $\text{RN}_3 = (4.843 - 2.271) 100\%/4.843 = 53.1\%$ and $\text{ROH} = 227.1\%/4.843 = 46.9\%$. From g.l.c., $\text{ROH} = 45.7 \pm 0.4\%$. From least-squares slope of $\log(V_\infty - V_t)$ against time, $k_{\text{obs}} = 4.71 \pm 0.07 \times 10^{-4} \text{ s}^{-1}$.

where NaN_3 was absent, to correspond to within 0.2% to the amount of substrate originally weighed out. In the Ph_2CHCl runs, plots of $\log(V_\infty - V_t)$ against time became slightly curved after one half-life has elapsed, as has been noted previously.²³ The linear portions of such plots were used in calculating k_{obs} . The average experimental error in all rate constants was $\pm 3\%$, and standard deviations in the slopes of $\log(V_\infty - V_t)$ against time

²¹ A. M. Ward, *J. Chem. Soc.*, 1927, 2285.

²² R. A. Bartsch, *J. Org. Chem.*, 1970, **35**, 1334.

²³ M. G. Church, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1940, 966.

plots were always less than this. A typical run is shown in Table 4.

Product Analysis.—The amount of RN_3 and Ph_2CHN_3 in infinity samples was calculated from $[\text{azide}]_\infty = [\text{substrate}]_0 - [\text{H}^+]_\infty$. The amount of Ph_2CHOH produced from Ph_2CHCl was calculated from $[\text{Ph}_2\text{CHOH}]_\infty = [\text{H}^+]_\infty$. The presence of small quantities of by-products having the same g.l.c. retention times as the components of the aforementioned octene mixture precluded the use of this titrimetric method in the estimation of ROH. The g.l.c. molar response of this product relative to ROME

was evaluated in separate experiments using the QF-1 column at 50° , and accordingly a known amount of this standard was added to the n-hexane extracts of ROMs infinity samples before g.l.c. analysis. It may be seen (Table 4, footnote *e*) that ROH(%) as calculated from the acid titre is significantly different from that determined by g.l.c.

I thank Professor P. B. D. de la Mare for helpful comments.

[3/1751 Received, 20th August, 1973]
