163. *Reaction Kinetics and the Walden Inversion. Part VIII.* Steric Course of Bimolecular Nucleophilic Substitution by an Anionic Substituting Agent in a Cationic Substrate.*

By S. H. Harvey, P. A. T. Hoye, E. D. Hughes, and Sir Christopher Ingold.

By application of the stereokinetic rule for S_N2 reactions of Type 1 (negative reagent, neutral substrate), for which type alone the rule is as yet well established, it is shown that 1-phenylethyl chloride, 1-phenylethanethiol, and the derived methyl sulphide, and dimethylsulphonium iodide, when of the same sign of rotation, have like configurations.

On the basis of this knowledge, it is shown that an S_N2 reaction of Type 2 (negative reagent, positive substrate), namely, that of the dimethylsulphonium ion with azide ion to give 1-phenylethyl azide (which is reducible to the amine), proceeds with practically quantitative inversion of configuration, despite the countervailing electrostatic forces.

It is a curious feature of current thought that the stereokinetic rule for S_N2 reactions[1]—the rule that inversion occurs in such independently of all constitutional details—has become generally accepted on little more than one-quarter of the proper evidential basis. There are four electrostatically distinct types of S_N2 reactions, as formulated below, and the rule is proved only for reactions of Type 1. There is evidence consistent with the rule for solvolytic reactions belonging to Type 3; but that is not proof; for whilst, in solvolysis, the S_N1 mechanism can often be established conclusively, and independently of stereochemical arguments, the S_N2 mechanism cannot be so easily proved and thus nearly always has the lower logical status of a judgment based on the totality of available indications. Since 1937 we have been slowly building up evidence on the rule in relation to Types 2, 3, and 4, and we now present our results concerning Type 2:

Type 1: $Y^- + RX \longrightarrow YR + X^-$
,, 2: $Y^- + RX^+ \longrightarrow YR + X$
,, 3: $Y + RX \longrightarrow YR^+ + X^-$
,, 4: $Y + RX^+ \longrightarrow YR^+ + X$

Type 2 provides the most crucial test that could be devised for the universality of the rule. For the incoming and the outgoing group have opposite ionic charges, and must electrostatically attract each other in the S_N2 transition state: here, if anywhere, we might find an S_N2 substitution with retention of configuration.

These considerations were prominent in the early history of the subject. In 1932 Meer and Polanyi suggested[2] that spatial orientation in substitution was electrostatically determined. In 1937 Cowdrey *et al.*[1] opposed that view, essentially on the theoretical ground that the exclusion principle would always defeat electrostatics. They supported their case on the practical side by citing Read and Walker's conversion,[3] in a reaction of Type 2, assumed to have the S_N2 mechanism, of trimethyl-*l*-piperitylammonium hydroxide, a *trans*-compound, into (+)-neopiperitol, which was said to be a *cis*-isomer.[4] But this citation was unlucky, because Macbeth and Shannon[5] showed in 1952 that Read and Walker's (+)-neopiperitol was a mixture, consisting of 70% of the *trans*- and 30% of the *cis*-isomer. It is easy to be wise now in pointing out that, because of the allylic system, Read and Walker's reaction may have pursued in part the S_N1 mechanism, which would, if the trimethylammonium group had the equatorial conformation, have produced

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* Part VII, preceding paper.

[1] Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252.

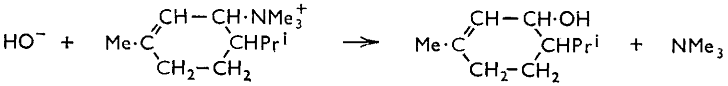
[2] Meer and Polanyi, *Z. phys. Chem.*, 1932, *B*, **19**, 164.

[3] Read and Walker, *J.*, 1934, 308.

[4] Read, " A Chapter in the Chemistry of the Essential Oils," Institute of Chemistry, 1936, p. 21.

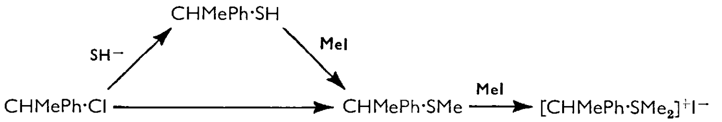
[5] Macbeth and Shannon, *J.*, 1952, 2852.

substitution with retention of configuration.[6] So, since 1952, there has been no practical evidence of the stereochemical direction of S_N2 substitutions of Type 2, apart from what we knew from unpublished work, which was, indeed, briefly mentioned in a publication [7] of 1953, and is now described in detail.



Our method involves traversing in three stretches a cyclic conversion path joining RX, RY, and RZ, where R is a hydrocarbon radical bound to X, Y, or Z through a non-cyclic, saturated carbon atom, which is asymmetric and is the only asymmetric centre present. Each of the three segments of path involves one and only one substitution at the asymmetric centre, which substitution is proved kinetically to proceed by mechanism S_N2. Each segment of path may involve other reactions also, but none of such must change any bond at the asymmetric centre. In two of the segments, say, RX to RY, and RX to RZ, the involved S_N2 substitutions both belong to Type 1, to which, as is well established, we can apply the stereokinetic rule, so connecting the relative sign of rotation with the relative configuration of RY and RX, and of RZ and RX, and therefore of RZ and RY. In the third segment of path, RY to RZ, the S_N2 substitution belongs to Type 2, and its stereochemistry will then follow from the observed rotations, and the now known connexion between relative rotation and relative configuration for RY and RZ. In our work, R was CHMePh, X was Cl, Y was SMe_2^+, and Z was NH_2.

The conversion of RX into RY was conducted in two ways, first,[7] as indicated by the upper variant of the following scheme, and later by the shorter path of the lower line, which alone will be described in detail. The longer path was useful for the purpose of obtaining the check on rotatory powers mentioned below.



The reaction of 1-phenylethyl chloride with sodium methyl sulphide in ethanol was followed through the disappearance of the MeS^- ion. The reaction displayed second-order kinetics, as is shown by the linearity of the plots in Fig. 1. This establishes that an S_N2 reaction is under observation. It appears from the rate-constants in Table 1 that the salt effect is small, as is expected for the S_N2 reaction of Type 1, in which ionic charges are neither produced nor destroyed.

TABLE 1. *Second-order rate constants* (k_2 *in* sec.$^{-1}$ *mole*$^{-1}$ *l.*) *of reaction of* 1-*phenylethyl chloride with sodium methyl sulphide in ethanol at* 35·0°.

Run	25	26	27	28	29	
$[MeSNa]_0$	0·126	0·193	0·095	0·126	0·144	
$[CHMePh·Cl]_0$	0·083	0·080	0·078	0·051	0·073	
10^3k_2	1·52	1·59	1·49	1·58	1·52	Mean 1·54

The sulphonium salt was prepared from the methyl 1-phenylethyl sulphide produced, by interaction with methyl iodide in nitromethane, in the dark and in the cold for as short a time as could be made preparatively convenient. The precautions mentioned were necessary when working with optically active material, because otherwise elemental iodine or tri-iodide ion may be generated, which racemises the sulphonium salt in nitromethane, and even in the solid state, so that, unless the preparations of salt were colourless, they were found to have lost some of their optical activity when first produced and also to be not fully optically stable.

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[6] Mills, *J.*, 1953, 260.

[7] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953, p. 380.

Lævorotatory 1-phenylethyl chloride gave in these reactions dextrorotatory 1-phenylethanethiol, methyl 1-phenylethyl sulphide, and dimethyl-1-phenylethylsulphonium iodide; and *vice versa.* It follows that the chloride, thiol, sulphide, and sulphonium iodide, when of the same sign of rotation, have like configurations. The rotations are mentioned below.

The second stretch, called RX to RZ above, of our cyclic conversion path is from 1-phenylethyl chloride to 1-phenylethylamine, according to the following scheme, in which an S_N2 substitution of Type 1 is followed by a reaction elsewhere than at the asymmetric centre:

$$\mathrm{CHMePh{\cdot}Cl} \xrightarrow[\mathrm{N_3^-}]{} \mathrm{CHMePh{\cdot}N_3} \xrightarrow[\mathrm{-Pt}]{\mathrm{H_2}} \mathrm{CHMePh{\cdot}NH_2}$$

The kinetic and optical work on this part of our route is described in the preceding paper. The conclusion from it is that 1-phenylethyl chloride and 1-phenylethylamine, when of the same sign of rotation, have like configurations.

FIG. 1. *Reaction,* $\mathrm{CHMePh{\cdot}Cl + SMe^- \longrightarrow CHMePh{\cdot}SMe + Cl^-}$, *in ethanol. Plots showing second-order form.*

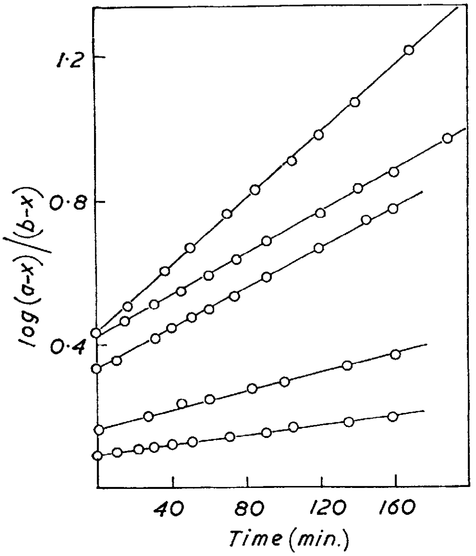
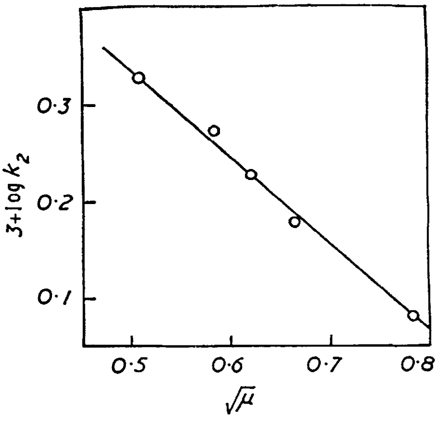


FIG. 2. *Reaction,* $\mathrm{CHMePh{\cdot}SMe_2^+ + N_3^- \longrightarrow CHMePhN_3 + SMe_2}$. *Brönsted plot of second-order rate* versus *ionic strength.*



The third stretch of our route is the conversion, RY to RZ, of the sulphonium ion into the amine by the process:

$$\mathrm{CHMePh{\cdot}SMe_2^+} \xrightarrow[\mathrm{N_3^-}]{} \mathrm{CHMePh{\cdot}N_3} \xrightarrow[\text{or }\mathrm{LiAlH_4}]{\mathrm{H_2\text{-}Pt}} \mathrm{CHMePh{\cdot}NH_2}$$

which contains the chief subject of our stereochemical interest, a nucleophilic substitution of Type 2, and otherwise only a reaction elsewhere than at the asymmetric centre.

Kinetic investigation of the reaction between the sulphonium iodide or chloride and sodium azide in " 80% " ethanol was preceded by experiments to detect and control side-reactions in these conditions, particularly as they might affect the production of dimethyl sulphide through which we intended to follow the main reaction. The two salts can conceivably interact among themselves in three ways, as follows,

$$\mathrm{N_3^- + CHMePh{\cdot}SMe_2^+} \longrightarrow \begin{cases} \mathrm{CHMePh{\cdot}N_3 + Me_2S} & \dots\dots (a) \\ \mathrm{CHMePh{\cdot}SMe + MeN_3} & \dots\dots (b) \\ \mathrm{CHPh{:}CH_2 + Me_2S + HN_3} & \dots\dots (c) \end{cases}$$

and, if solvolysis is allowed for, they could react in two more ways, here formulated only for hydrolysis, though this would be accompanied by corresponding alcoholytic processes:

$$H_2O + CHMePh{\cdot}SMe_2^+ \longrightarrow CHMePh{\cdot}OH + Me_2S + H^+ \quad . \; . \; . \; . \; . \; . \; . \quad (d)$$

$$(+\,H_2O)\Big\uparrow(-X^-)$$

$$X^- + CHMePh{\cdot}SMe_2^+ \longrightarrow CHMePh{\cdot}X + Me_2S\ (X = Cl\ \text{or}\ I) \quad . \; . \; . \; . \; . \quad (e)$$

Since the solvolysis of 1-phenylethyl chloride and iodide is fairly rapid, we should obtain the products resulting from attack of halide ion of the sulphonium ion in the form of solvolysis products.

As to reactions (*a*), (*b*), and (*c*), a preparative study showed that the high-boiling product contained less than 0·2% of methyl 1-phenylethyl sulphide; and that no styrene could be detected. Thus, apart possibly from the reactions involving solvolysis, the production of dimethyl sulphide measures essentially reaction (*a*).

The reactions (*d*) and (*e*) were examined kinetically, in solutions from which the sodium azide had been left out. At the sulphonium salt concentrations relevant to our kinetic runs in the presence of sodium azide, and in the same solvent at the same temperature, reaction (*e*) with iodide ions was more important either than (*e*) with chloride ions, or than reaction (*d*), whilst the last two reactions were themselves comparable in importance. The reactions had approximately an overall first-order form, because the rapid solvolysis of the 1-phenylethyl halides, particularly the iodide, led to a nearly constant concentration of halide ions. These results determined that, in the final series of kinetic runs on the reaction of the sulphonium ion with azide ion, we should employ the sulphonium chloride rather than the sulphonium iodide. Moreover, the approximate rates of these solvolytic processes being known, it was easy so to set the concentrations of the sulphonium chloride and the sodium azide in this final series of runs that 95 ± 2% of the production of dimethyl sulphide would be attributable to reaction (*a*).

TABLE 2. *Integrated second-order rate constants ($\bar{k}_2$ in sec.$^{-1}$ mole^{-1} l.) obtained during a run of the reaction of dimethyl-*1*-phenylethylsulphonium chloride with sodium azide in " 80% " ethanol at* 55·2°.

(*Run* 41: Initially, $[CHMePh{\cdot}SMe_2^+Cl^-]$ = 0·095M and $[NaN_3]$ = 0·521M. The Me_2S in samples of 16·23 ml. was weighed as $Me_2S,2HgCl_2$.)

Time (min.)	$Me_2SHg_2Cl_4$ (g.)	μ	$10^3\bar{k}_2$
0	0·015	0·616	—
10	0·277	0·5627	1·11
18	0·450	0·5273	1·17
24	0·552	0·5065	1·21
30	0·611	0·4945	1·16
51	0·786	0·4587	1·21
∞	0·951	0·4251	—

TABLE 3. *Mean second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of reaction of dimethyl-*1*-phenylethylsulphonium chloride with sodium azide in " 80% " ethanol at* 55·2°.

Run	$[CHMePh{\cdot}SMe_2^+Cl^-]_0$	$[Na^+N_3^-]_0$	[Total salts]$_0$	10^3k_2
35	0·105	0·151	0·256	2·14
36	0·112	0·234	0·346	1·88
37	0·155	0·229	0·384	1·69
38	0·104	0·336	0·440	1·52
41	0·095	0·520	0·615	1·17

These runs, which were conducted in " 80% " ethanol at 55·2°, gave fairly good second-order rate-constants, showing a small but consistent tendency to rise as the runs progressed, as illustrated in Table 2. This establishes that an S_N2 reaction is proceeding, the small rise in the integrated rate constant being expected for such a reaction of Type 2, which destroys ionic charges, and therefore must display a negative salt effect; for the ionic strength diminishes as reaction progresses. A much clearer demonstration of the salt effect is found in the comparison of mean rate constants of different runs, set out in Table 3. The parameter controlling the variation in rate is obviously the sum of the two salt concentrations, that is, the ionic strength; and in fact, the plot of the logarithm of the rate constant *versus* the square root of the ionic strength was linear, in accordance with Brönsted's law, as Fig. 2 shows, the line having the theoretically reasonable slope of $-0{\cdot}9$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$.

The second step in the conversion of the 1-phenylethylsulphonium ion into 1-phenylethylamine, *viz.*, the reduction of the azide, formed under the conditions of the kinetic experiments, was accomplished either with hydrogen and Adams's catalyst as described in the preceding paper or by means of lithium aluminium hydride.

Dextrorotatory sulphonium iodide, on conversion thus through the sulphonium chloride and 1-phenylethyl azide, gave lævorotatory 1-phenylethylamine; and optically *vice versa*. Therefore the S_N2 substitution of Type 2, by which the 1-phenylethyl sulphonium ion, by reaction with azide ion, gave 1-phenylethyl azide must have involved stereochemical inversion.

We now develop this conclusion quantitatively. Downer and Kenyon fully resolved 1-phenylethyl alcohol,[8] and showed that it had α_D^{17} (max.) 44·2° (all values of α in this paper refer to l 1 dm.). Gerrard discovered [9] how to convert this alcohol into the chloride with very little if any racemisation, by treating it with phosphoryl chloride and pyridine in carbon disulphide; he thus obtained chloride of α_D^{16} −99·6°. Various indications have since been obtained, and we add two more in this paper, that Gerrard's rotation was substantially a maximum. From chloride of α_D^{20} 56·60°, we obtained, by the one-step process of treatment with sodium methyl sulphide under conditions kinetically controlled to secure a pure bimolecular reaction, methyl 1-phenylethyl sulphide with α_D^{20} −88·54°. From this result it can be computed that the sulphide has α_D^{20} (max.) 155·8°.

A check on this value can be obtained. Holmberg [10] fully resolved (1-phenylethylthio)acetic acid, and from the active acid obtained by alkaline hydrolysis 1-phenylethanethiol of α_D^{20} −107·9°. We should not expect this hydrolysis to be accompanied by significant racemisation. In our two-step method of passing from 1-phenylethyl chloride into the methyl sulphide, we converted 1-phenylethanethiol of α_D^{20} +10·94°, by treatment of its potassium salt with methyl iodide, into methyl 1-phenylethyl sulphide of α_D^{20} +15·44°. No racemisation is expected to accompany this methylation. On the assumption that no racemisation accompanied either of these reactions, a value results for the maximum rotation of methyl 1-phenylethyl sulphide: it is α_D^{20} 152·3°, in good agreement with the value given above. This result supports Gerrard's value of the rotatory power of 1-phenylethyl chloride.

From a sample of methyl 1-phenylethyl sulphide having α_D^{20} +22·66°, we obtained a colourless, optically stable sample (cf. p. 801) of the dimethylsulphonium iodide with $[\alpha]_D^{20}$ +10·7° in ethanol. The maximum rotation of the sulphonium salt is therefore $[\alpha]_D^{20}$ 73·6° in ethanol.

From the same sample of the sulphonium iodide, by conversion into the sulphonium chloride, and interaction of this with sodium azide under conditions kinetically controlled as described above, and then reduction of the 1-phenylethyl azide formed, we obtained 1-phenylethylamine having α_D^{20} −5·50°. Sulphonium salt of maximum rotatory power would therefore have given amine having α_D^{20} −36·5°. Holmberg's value [11] for the rotation of the amine is α_D^{19} (max.) −38·7°. Our amine was therefore produced with 94% of its maximum activity, and the dimethyl-1-phenylethylsulphonium azide must have been converted into 1-phenylethyl azide with 97% of inversion, and 3% of retention of configuration.

The deficiency from 100% of inversion is easily explained. We know that the side-reaction, labelled (*e*) on p. 803, accounts for about 2—4% of the total reaction of

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[8] Downer and Kenyon, *J.*, 1939, 1156.

[9] Gerrard, *J.*, 1946, 741.

[10] Holmberg, *Arkiv Kemi, Min., Geol.*, 1939, **13**, *A*, 8.

[11] Holmberg, *Ber.*, 1912, **45**, 999.

sulphonium salt occurring in our conditions. In the presence of sodium azide, the 1-phenylethyl chloride formed in reaction (*e*) would not be wholly solvolysed, as represented on p. 803, but would be partly solvolysed, and largely converted into 1-phenylethyl azide. The azide produced in this way, having been formed from the sulphonium ion by two substitutions, each with inversion, would, in comparison with the sulphonium ion, have a retained configuration. Incidentally, we again find support for Gerrard's value of the rotatory power of 1-phenylethyl chloride.

We conclude that, the countervailing electrostatic situation notwithstanding, S_N2 substitutions of Type 2 obey, to a very close approximation, the usual stereokinetic rule prescribing quantitative inversion.

EXPERIMENTAL

Preparations.—1-Phenylethyl alcohol was resolved, and the inactive and active alcohols were converted into chlorides by well-known methods. Inactive and active chlorides were treated in methanol at 60° with sodium hydrogen sulphide (prepared by first dissolving sodium in the solvent and then saturating it with hydrogen sulphide) to give the thiol, b. p. 93°/17 mm. Inactive and active samples of this thiol were methylated with sodium ethoxide and methyl iodide in ethanol, to give the methyl sulphide, b. p. 91—92°/12 mm., 98°/18 mm., n_D^{25} 1·5478, n_D^{20} 1·0055 (Found: C, 70·8; H, 7·5. Calc. for $C_9H_{12}S$: C, 71·0; H, 7·9%). The same sulphide was prepared directly from the chloride and sodium methyl sulphide under conditions resembling those of the kinetic experiments on this reaction (cf. Table 1), *e.g.*, by heating a solution prepared from 1-phenylethyl chloride (21·9 g.) sodium (5·78 g.), methanethiol (12 g.), and ethyl alcohol (1 l.), therefore originally 0·15M in the chloride and 0·25M in the sodium methyl sulphide, at 35·0° for 48 hr. After the alcoholic solution had been poured into aqueous sodium chloride, the dialkyl sulphide was collected in ether. Inactive and active samples of the sulphide were methylated in conditions in which yield was sacrificed to purity and optical stability, as explained on p. 801; for example, a solution of the sulphide (66 g.) and methyl iodide (65 g.) in nitromethane (55 g.) was kept in the dark at 13° for 2 hr., and the sulphonium iodide was precipitated and washed with ether (yield 30%) (Found, for the picrate: C, 48·4; H, 4·2. Calc. for $C_{16}H_{19}O_7N_3S$: C, 48·6; H, 4·3%). The solvolysis of the sulphonium iodide, and of the sulphonium chloride made from it with the aid of silver chloride, as well as the reaction of both sulphonium salts with sodium azide, always in " 80% " ethanol (a mixture of 4 vols. of ethanol with 1 vol. of water) at 55·2°, were all examined preparatively, the products being isolated by collection in pentane after pouring of the alcoholic solutions into saturated aqueous calcium chloride. Dimethyl sulphide was removed by distillation, and the appropriate higher fractions were tested for styrene by means of bromine and for methyl 1-phenylethyl sulphide with the aid of mercuric chloride, with which it readily forms an insoluble complex. No styrene, and not more than 0·2% of methyl 1-phenylethyl sulphide, was detected in any experiment. 1-*Phenylethyl azide* was isolated having b. p. 76—80°/18 mm. (Found: C, 65·9; H, 6·8. $C_8H_9N_3$ requires C, 65·3; H, 6·1%). This analysis, and perhaps the isolation, should have been repeated, but we did not do it because of the danger. Our usual procedure was, in our earlier experiments, to collect the organic azide in pentane, evaporate the pentane, and then reduce the residue in methyl alcohol with hydrogen (10 atm.) and Adams's platinum catalyst, and, in our later work, to collect the azide in ether, concentrate the solution, and then add this slowly to an ethereal solution of an excess of lithium aluminium hydride, the excess of which was afterwards destroyed by water. The acidified aqueous solution of 1-phenylethylamine was extracted with ether or pentane, and then basified, and the amine was extracted with one of these solvents and distilled (b. p. 83°/20 mm.) (Found: C, 79·1; H, 8·9. Calc. for $C_8H_{11}N$: C, 79·3; H, 9·1%). The benzoate, crystallised from aqueous ethanol, had m. p. 121° (Found: C, 80·2; H, 6·7. Calc. for $C_{15}H_{17}O_2N$: C, 80·0; H, 6·7%). In experiments on the conversion of the optically active sulphonium chloride into the azide, and thence into the amine, the conditions of the kinetic experiments were imitated. Thus, a solution (800 ml.) in " 80% " ethyl alcohol, 0·096M in the sulphonium chloride, and 0·53M in sodium azide, was heated at 55·2° for 3 hr., and the product was worked up as described.

Quantitative Work.—The kinetics of the reaction between 1-phenylethyl chloride and sodium methyl sulphide in ethanol at 35·0° were followed by the disappearance of the MeS^- ion as measured acidimetrically. Sealed tubes were used. Each tube was broken under carbon tetrachloride and water, and the carbon tetrachloride layer was washed twice with water. The combined aqueous solutions were titrated with 0·02N-perchloric acid, a mixed indicator of Bromocresol Green and Methyl Red being used. The time of removal from the thermostat of the first tube was taken as the time-zero, and the concentrations of the reactants at that time, *a* and *b* in the formula

$$\bar{k}_2 = \{2{\cdot}303/(a - b)t\} \log \{b(a - x)/a(b - x)\}$$

were calculated from the amounts taken, and the amounts that had reacted at the time-zero. About 85—95% of the reaction was followed, and the values of $\bar{k}_2$ within each run were so free from drift and casual error that it is unnecessary to illustrate them. A summary of mean constants is in Table 1.

The kinetics of this reaction of dimethyl-1-phenylethylsulphonium chloride with sodium azide at 55·2° in "80%" ethanol (a mixture made from 4 vols. of ethanol and 1 vol. of water) were followed by gravimetric determination of methyl sulphide formed, by means of its mercuric chloride complex, Me_2S,Hg_2Cl_4. Sealed tubes were used, the volumes of their contents being adjusted according to the concentration of sulphonium salt, to correspond at "infinite" time to about 2 g. of complex. The tubes were broken under carbon tetrachloride and water, and the carbon tetrachloride solution, after having been washed with water, was shaken with saturated aqueous mercuric chloride, and the complex was collected, dried, in an evacuated desiccator over calcium chloride, and weighed. As Burgess [12] has recorded, the precipitation of dimethyl sulphide as the complex is incomplete unless the mercuric chloride solution is still nearly saturated after the precipitation. We used twice the proportion of mercuric chloride employed by Burgess, and we kept the mercuric chloride solution, before mixing, at a temperature above that of the carbon tetrachloride solution by 1—3°, depending on the weight of complex to be precipitated, so that, after mixing, there would be a decrease of the solubility of mercuric chloride, which would be only a little less than corresponded to the amount taken up to form the complex. The time of removal from the thermostat of the tube first removed was taken as the time zero. A determination at "infinite" time (10 half-lives) gave the amount of sulphonium salt originally introduced. The *a* and *b* of the second-order rate formula were computed from this, and the weight of sodium azide taken, after allowance for the reaction that had already occurred at the time-zero. The second-order rate constants showed some scatter, combined with a small upward drift, as illustrated in Table 2. Mean-rate constants are given in Table 3.

The more important measurements of rotatory power have already been recorded (p. 804).

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[*Received, August 20th,* 1959.]

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[12] J. S. Burgess, Thesis, London, 1953.