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Eliminations Promoted by Thiolate lons. Part III.¹ Reactions of t-Butyl Chloride and t-Butyldimethylsulphonium lodide

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The effect of the leaving group on the relative reactivities of benzenethiolate and alkoxide ions in bimolecular eliminations from t-butyl compounds is investigated. The substrates studied are t-butyl chloride and t-butyldimethylsulphonium iodide. There is a correlation between the relative reactivities of these bases and Brönsted ß coefficients, obtained by using substituted benzenethiolates as bases, for the two reaction series. The variation of the rate ratio with the change in leaving group is explained in terms of alterations in the nature of the E2 transition states.

INVESTIGATIONS of the relative reactivities of benzenethiolate and alkoxide ions in effecting bimolecular elimination reactions with cyclohexyl halides and cyclotoluene-*p*-sulphonate,¹ aa-dimethylphenethyl hexyl chloride and the corresponding dimethylsulphonium salt and methyl sulphone,² and DDT ³ have shown that the thiolate-alkoxide rate ratio is sensitive to the nature of the E2 transition state.⁴ Results of a similar investigation on the t-butyl system reported in this Paper are not fundamentally different from those of Bunnett and Baciocchi, who studied the related aa-dimethylphenethyl system.²

t-Butyl chloride is dehydrochlorinated by benzenethiolate in ethanol 10 times faster that it undergoes a second-order reaction with ethoxide in this solvent.⁵ However, no olefin proportion was obtained for the latter reaction, so this reactivity ratio of 10 is not necessarily the ratio for E2 reaction. We now extend the work of de la Mare and Vernon and obtain a more accurate value of this E2 rate ratio. The reactions of the tbutyldimethylsulphonium ion are similarly investigated. We diagnose the nature of the E2 transition states by using, as before, the Brönsted catalysis law.

RESULTS

Alkoxide-promoted Eliminations.—(a) t-Butyl chloride. Even in strongly alkaline solution it is difficult to isolate a clean second-order mode of decomposition of tertiary alkyl halides because of the incursion of relatively fast unimolecular (E1 and S_N 1) reactions.⁶ Accordingly, we have measured the pseudo-first-order rate coefficients of the decomposition of t-butyl chloride in alkaline ethanol, and have corrected for the concomitant unimolecular reactions by using the specific rate of solvolysis of the halide in neutral ethanol, which is assumed to be a purely unimolecular reaction. Olefin proportions have been similarly corrected. In order to extract second-order rate constants for the E2reaction we have followed the assumptions of Bunnett et al.7 and have used their general method.

The raw, first-order, rate constants and olefin proportions are shown in Table 1. Specific rates derived from these quantities are presented in Table 2.

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- 1948, 2065.

The small overall decrease in k(E1) and $k(S_N1)$ with increasing alkali concentration may be an example of lyate ion retardation.8 The specific rate of the bimolecular elimination is effectively constant over the range of alkali concentration.

ТΑ	BLE	1

Specific rates and olefin proportions of the reactions of t-butyl chloride in initially neutral and in alkaline ethanol at 45.0°

[Bu ^t Cl]	[NaOEt]	10 ⁸ k ₁ (sec. ⁻¹)	% Olefin
0.1011		1.35	22.8
0.0501	0.3502	3.03	92.6
0.0524	0.4926	3.82	93·9
0.0671	0.7347	4.99	96.3

Table	2
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Specific rates derived from data in Table 1

[NaOEt]	$10^{6}k$ (E2) (1. mole ⁻¹ sec. ⁻¹)	$10^{8}k$ (E1) (sec. ⁻¹)	$10^{7}k (S_{\rm N}1)$ (sec. ⁻¹)
0.3502	4.45	2.2	`6·7 ´
0.4926	4.53	$2 \cdot 3$	6.9
0.7347	4.69	1.9	5.4

(b) t-Butyldimethylsulphonium iodide. Solvolytic reactions do not sensibly interfere with the measurement of second-order specific rates of decomposition of this substrate in alkaline solution.9 All reactions have been assumed to be 100% elimination, on the basis of a previous report.¹⁰

TABLE 3

of t-butyldimethylsulphonium iodide The reaction (ca. 0.02N) and alkoxide ions (ca. 0.08N) in ethanol and methanol

(a)	Solvent EtOH:			
	Temp. (°c)	25.0	35.0	45·0
	$10^{5}k_{2}$ (l. mole ⁻¹ sec. ⁻¹)	247	1020	3260
(b)	Solvent MeOH:			
	Temp. (°c)	25.0		45.0
	$10^{5}k_{\bullet}$ (l. mole ⁻¹ sec. ⁻¹)	37.2		498

The activation parameters of the OEt-/EtOH reaction are: ΔH^* , 23.9 kcal. mole⁻¹; ΔS^* , 7.8 cal. deg.⁻¹ mole⁻¹ and of the OMe⁻/MeOH reaction are: ΔH^* , 23.6 kcal. mole⁻¹; ΔS^* , 2.9 cal. deg.⁻¹ mole.⁻¹.

Benzenethiolate-promoted Eliminations.-(a) t-Butyl chloride. The reactions between t-butyl chloride and substituted benzenethiolates $(p-RC_6H_4S^-)$ were approximately

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second-order except for $R = NO_2$; then there was a small upward drift in the observed rate constants as a result of the solvolytic reactions. The individual observed specific rates of this reaction were corrected using the formula:

$$k_2 = k_2$$
 (obs.) - k_1 /[base]

in which k_2 is the true second-order specific rate of base attack and k_1 is the rate coefficient of the solvolytic reaction in neutral ethanol. The mean k_2 values in the other runs were likewise corrected (Table 4). Values of the dissected E2 rate constants are shown in Table 5.

TABLE 4

Specific rates (in 1. mole⁻¹ sec.⁻¹) and olefin proportions of the reactions between t-butyl chloride (*ca*. 0.08M) and benzenethiolates (p-RC₆H₄S⁻) in ethanol at 45.0°

R	[Base]	$10^{5}k_{2}$ (obs.)	10 ⁵ k ₂	% Olefin
Me	0.2029	5.96	5.30	95.0
н	0.2065	4.51	4.06	93·4
Br	0.2425	3.73	3.18	92 ·1
NO ₂	0.1737	2.08 - 2.46	1.30	89.1

TABLE 5

Rate constants derived from data in Table 4

R	Me	\mathbf{H}	Br	NO_2
$10^{5}k$ (E2) (l. mole ⁻¹ sec. ⁻¹)	 5.03	3.79	2.93	1.16

(b) *t-Butyldimethylsulphonium iodide*. It was not necessary to correct for solvolysis. Olefin proportions as determined during the course of kinetic runs were effectively constant. However, the large error inherent in determining small quantities of olefin under the concentration conditions of the kinetic runs necessitated separate productdetermining experiments, in which reactant concentrations were chosen so as to minimise experimental error. Total salt concentrations in these experiments were adjusted to those used in the kinetic runs by the addition of inert salt. The resulting olefin proportions agreed closely with those obtained from kinetic runs, but, in Table 6, only the former are reported.

TABLE 6

Specific rates and olefin proportions of the reactions between t-butyldimethylsulphonium iodide (ca. 0.02N) and benzenethiolates (p-RC₆H4S⁻) (ca. 0.06N) in ethanol and methanol

			10 ⁵ k ₂	% Olefin
Solvent	R	Temp.	(l. mole ⁻¹ sec. ⁻¹)	(±0·3)
EtOH	Me	25.0°	933	10.7
,,	\mathbf{H}	25.0	651	10.0
.,	\mathbf{Br}	25.0	459	7.0 ± 0.2
,,	NO,	25.0	124	2.9 ± 0.1
	н	35.0	2460	10.6
	н	45·0	8440	10.9
MeOH	н	25.0	65.0	10.1
	н	35.0	256	10.5
,,	н	45 ·0	964	11.1

TABLE 7

E2 and $S_{\rm N}2$ rate constants dissected from data in Table 6 on reactions of *p*-substituted benzenethiolates in ethanol at $25 \cdot 0^{\circ}$

R		Me	\mathbf{H}	Br	NO2
$10^{5}k$ (E2) (l. mole ⁻¹ sec. ⁻¹) .	••	99.8	65.1	32.1	3.60
$10^{5}k$ (S _N 2) (l. mole ⁻¹ sec. ⁻¹).	•••	833	586	427	120

TABLE 8

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Variation of E2 and $S_N 2$ specific rates of benzenethiolatepromoted reactions (R = H) with temperature, taken from data in Table 6

Solvent EtOH:			
Temp. (°c)	25.0	35.0	45 ·0
$10^{5}k^{-}(E2)$ (l. mole ⁻¹ sec. ⁻¹)	65·1	261	962
$10^{5}k (S_{N}2)$ (l. mole ⁻¹ sec. ⁻¹)	586	2200	7480
Solvent MeOH:			
Temp. (°c)	25.0	35.0	45 ·0
$10^{5}k^{-}(E2)$ (l. mole ⁻¹ sec. ⁻¹)	6.65	26.9	107
$10^{5}k$ (S _N 2) (l. mole ⁻¹ sec. ⁻¹)	58.4	229	857

Activation parameters of the E2 and S_N2 components of the sulphonium ion-benzenethiolate reaction, calculated from data in Table 8, are shown in Table 9.

TABLE 9

Acitvation parameters of the t-butyldimethylsulphonium iodide-benzenethiolate reactions.

Solvent	Reaction	ΔH^* (kcal. mole ⁻¹)	ΔS^* (cal. deg. ⁻¹ mole ⁻¹)
EtOH	E2	24.1	5.9
,,	$S_{N}2$	24.0	10.2
MeOH	E2	26.3	4.2
,,	$S_{N}2$	24.5	6.8

Primary Salt Effects on Rates of Reaction of the Sulphonium Salt.—The possibility that the alkoxide- and benzenethiolate-promoted reactions would exhibit different ionic strength effects was investigated. Ionic strengths were varied by the addition of sodium iodide. Results are presented in Table 10.

TABLE 10

Effect of ionic strength on specific rates of reaction of t-butyldimethyl sulphonium iodide with ethoxide and benzenethiolate in ethanol at 25.0°

				10°R.	
Base	[Bu ^t SMe ₂ +]	[Base]	[NaI]	(l. mole ⁻¹ sec. ⁻¹)	% Olefin
OEt-	0.0128	0.0326	0.0200	323	100 *
,,	0.0119	0.0778		247	100 *
,,	0.00996	0.0304	0.0600	208	100 *
PhS-	0.0183	0.0587		651	10.0
,,	0.0107	0.0317	0.0408	549	9.8
,,	0.0109	0.0326	0.0591	438	10.3
	0.0109	0.0327	0.0814	336	10.1
		* Ass	umed (re	f. 10).	

Plots of log k_2 against \sqrt{I} for the reactions of both bases are linear. The olefin proportion is apparently constant over the range of ionic strengths used in the benzenethiolatepromoted reactions. A similar situation has been reported for $E2/S_N2$ reactions of other 'onium salts with anionic bases.¹¹ On extrapolating the rate data in Table 10 to zero ionic strength and assuming a constant 10.0% proportion of olefin in the benzenethiolate-promoted reaction, we obtain the following rate constants for bimolecular elimination at I = 0:

Ethoxide: $10^{5}h(E2) = 151$ l. mole⁻¹ sec.⁻¹ at $25 \cdot 0^{\circ}$ Benzenethiolate: $10^{5}h(E2) = 46 \cdot 8$ l. mole⁻¹ sec.⁻¹ at $25 \cdot 0^{\circ}$

The slopes of the log k_2 against \sqrt{I} plots are -2.8 and -3.4 for the ethoxide- and benzenethiolate-promoted reactions, respectively. The theoretical Debye-Hückel-Bjërum slope for reactions of this type (-2A where A is the Debye-Hückel coefficient) is -5.92 for ethanol at 25°. The discrepancy between theory and experiment has been re-

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ported in other investigations of reactions of 'onium salts with anionic bases.11,12

Solvent Effects on Rates of Reaction of the Sulphonium Salt. -Specific rates of the reaction between benzenethiolate and the sulphonium salt in ethanolic and methanolic media decreased as water was added to the solvents (Table 11). There was a similar decrease in the rates of the alkoxidepromoted reactions as water was added to alkaline ethanolic and methanolic solvents (Table 12)

TABLE 11

Specific rates and olefin proportions of the reaction between benzenethiolate (ca. 0.06N) and t-butyldimethylsulphonium iodide (ca. 0.02N) in alcoholic and aqueousalcoholic solvents

Vol. % of H ₂ O	0	10	20
	EtOH/H ₂ O at 25.0°		
$10^{5}k_{2}$ (l. mole ⁻¹ sec. ⁻¹)	651	194	30.4
% Olefin	10.0	9.9	9.1
	MeOH/H ₂ O at 45.0°		
$10^{5}k_{2}$ (l. mole ⁻¹ sec. ⁻¹)	964	197	44 ·9
% Olefin	11.1	10.4	10.4

TABLE 12

Specific rates of the elimination reaction between the lyate ions of the solvent (ca. 0.08N) and t-butyldimethylsulphonium iodide (ca. 0.02N) in alcoholic and aqueousalcoholic solvents at 45.0°

Vol. % of H ₂ O	0	10	20
EtOH-H ₂ O: 10 ⁵ k ₂ (l. mole ⁻¹ sec. ⁻¹)	3260	404	$63 \cdot 2$
MeOH- $H_2O: 10^5k_2$ (,,)	498	84.0	11.4

Reactions of t-Butyl Methyl Sulphone.-It was hoped that an examination of the reactions of this substrate would provide a comparison with the results obtained from reactions of $\alpha\alpha$ -dimethylphenethyl methyl sulphone by Bunnett and Baciocchi.² t-Butyl methyl sulphone underwent a slow reaction, predominantly elimination, with ethoxide in ethanol at 96° ($k_2 = ca. 10^{-7} l. mole^{-1} sec.^{-1}$) but no reaction with benzenethiolate could be detected at this temperature. The low reactivity of the substrate caused the investigation to be discontinued.

DISCUSSION

The Brönsted Relationship and Transition State Character .-- On employing the previously determined basicity constants of the benzenethiolates,³ we find that the rate data in Tables 5 and 7 obey the Brönsted catalysis law. As before, we interpret the Brönsted slopes (β) as being measures of the degree of proton transfer from the substrate to the base in E2 transition states or as measures of the degree of bond-making in $S_{\rm N}2$ transition states. The relevant parameters are given in Table 13.

We see that increasing the electronegativity and the tightness of binding of the leaving group results in a shift of E2 transition state character from the E1-type (chloride) to a central type (sulphonium salt). The β

Soc., 1956, 78, 2915.

Brönsted parameters for the reactions of t-butyl chloride and t-butyldimethylsulphonium iodide with benzenethiolate in ethanol

Substrate	Temp.	Reaction	β	$\log G$
Bu ^t Cl	45·0°	E2	0.17	-2.63
Bu ^t SMe ₂ +	$25 \cdot 0$	E2	0.46	1.41
,,	25.0	S N2	0.27	0.52

parameter of the $S_N 2$ reaction of the sulphonium salt with benzenethiolate (displacement of t-butyl methyl sulphide from a methyl group-see Experimental section) is lower than that of the E2 reaction as is the case in other $E2/S_N2$ reactions.^{1,13} The fact that elimination and substitution reactions occur in the t-butyl and methyl moieties of the substrate, respectively, is good evidence against the operation of a "merged" substitution-elimination mechanism ¹⁴ which has been suggested as an explanation of the previously regarded anomalous reactivity of benzenethiolate towards t-butyl chloride.15,16

That the $S_N 2$ reaction of the sulphonium salt is (1) and not (2) shows that the polar and steric factors which

F

Ph

$$PhS^- + Bu^{t}SMe_2^+ - PhSMe + Bu^{t}SMe$$
 (1)

$$S^- + Bu^t SMe_2^+ \longrightarrow PhSBu^t + SMe_2$$
 (2)

cause benzenethiolate to be ineffective in the substitution reaction with t-butyl chloride are also operative in retarding substitution in the t-butyl group of the sulphonium salt, diverting it to the more accessible methyl groups. In its substitution reaction with ethanethiolate, the 1,1-dimethyl-2-phenethyldimethylsulphonium ion behaves similarly.²

Relative Reactivities of Benzenethiolate and Alkoxide.---Benzenethiolate is 8.3 times more reactive than ethoxide in dehydrochlorinating t-butyl chloride. When the leaving group is changed from chloride to dimethyl sulphide, the reactivity order of the two nucleophiles is reversed and the benzenethiolate: ethoxide rate ratio for E2 reaction at zero ionic strength becomes 0.31:1. The decrease in the ratio and the reversal in the reactivity order is similar to that reported by Bunnett and Baciocchi.² It is explicable in terms of the shift in E2transition state character from an E1-type transition state for which rates are relatively insensitive to the basic strengths of nucleophiles but may be sensitive to other factors if they are sufficiently prominent (such as the polarisability of thiolate ions) to a central or E1cBtype transition state for which the sensitivity of rate to basic strength apparently outweighs other factors determining nucleophilic reactivity.

Solvents Effects .--- The Hughes-Ingold theory of solvent action predicts that reactions of charge-type 3 (positive substrate, negative reagent) should be retarded as solvent polarity is increased.¹⁷ This is qualitatively verified for the benzenethiolate-sulphonium salt reaction. The

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reactions of benzenethiolate with neutral substrates in $E2^{3,18}$ and S_N2^{19} processes are not in accordance with the predictions of the Hughes-Ingold theory, but it is clear that solvation effects are dominant when the substrate is an ionic species, for there is a greater amount of charge separation on going from the initial to the transition states.

The large rate decrease observed when water is added to alkaline ethanolic and methanolic solvents may also be largely attributed to stabilisation of the initial state by increasing solvation. Shifts in alkoxide-hydroxide equilibria (3) may also contribute to the rate decrease

$$OR^- + H_2O \xrightarrow{} ROH + OH^-$$
(3)

but unlike the situation met with in $S_{\rm N}2^{19,20}$ and E2²¹ reactions of neutral substrates in alkaline alcoholic media where effects due to this equilibrium are thought to dominate rate changes, solvation effects appear to be more important when ionic substrates are used, for the rate decreases of the latter reactions on adding water to alkaline alcoholic solvents are much larger than those observed for the reactions of neutral substrates. However, shifts in alkoxide-hydroxide equilibria appear to reinforce the rate changes as water is added to alcohol. The rate decrease associated with ethanol-water solvents is greater than that observed in the corresponding methanol-water solvents. In media of low water content, ethoxide is more extensively hydrolysed to the less reactive hydroxide ion than is methoxide hydrolysed to hydroxide.¹⁹ Hence the reinforcing effect should be greater in ethanol-water mixtures and this is observed.

EXPERIMENTAL

Materials .- t-Butyl chloride (B.D.H.) was dried and carefully fractionated. Equimolar quantities of methyl iodide and t-butyl methyl sulphide were mixed in nitromethane in the preparation of the sulphonium salt. After 12 hr. in the dark, the product crystals were collected and washed with dry ether. They were then dissolved in the minimum quantity of cold ethanol and reprecipitated by the addition of dry ether several times, and had m. p. 159.5-160° (decomp.) (lit.,²² m. p. 159.5-160.2°). The t-butyl methyl sulphide was prepared from 2-methylpropane-2-thiol and dimethyl sulphate by the method of Vogel and Cowan.²³ Oxidation of t-butyl methyl sulphide with excess of hydrogen peroxide in glacial acetic acid afforded t-butyl methyl sulphone, which, on recrystallisation from benzene-ether (50: 50), had m. p. 83.5-84° (lit.,²⁴ 84.3-84.5°).

Thiophenols were prepared and purified as previously described.³ Methanol and ethanol were dried in the usual way and substrate and base solutions were made up for kinetic runs as before.³

Reaction Products .- de la Mare and Vernon have de-¹⁸ E. L. Eliel and R. S. Ro, J. Amer. Chem. Soc., 1957, 79,

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scribed the isolation and characterisation of 2-methylpropene as principal product of the t-butyl chloridebenzenethiolate reaction. In an apparatus continually swept with nitrogen and protected from contamination by carbon dioxide, 24 g. of the sulphonium salt and benzenethiolate (from 22 g. of benzenethiol) in a litre of ethanol were allowed to react at 0° and, during 24 hr., 0.5 g. of volatile product was collected in a cold-trap. This product was allowed to evaporate into a solution of bromine in carbon tetrachloride and, after removal of the residual bromine, 1,2-dibromo-2-methylpropane (2.0 g.) was obtained, b. p. 149—151°/758 mm.; $n_{\rm p}^{25}$ 1·5066 (lit.,⁵ b. p., 148—150°/ 766 mm.; $n_{\rm p}^{25}$ 1·5070). The weight of dibromide corresponded to an olefin yield of at least 8.8%. The reaction mixture was then concentrated by distilling most of the solvent and was taken up in ether. After being washed with dilute aqueous sodium hydroxide to remove benzenethiol, and with water, the extract was dried and the ether removed. The liquid residue was fractionated and there were obtained (9 g. 86.5%) t-butyl methyl sulphide, b. p. $101-102^{\circ}/759 \text{ mm.}$; $n_{\rm p}^{25}$ 1.4454 (lit.,²³ b. p. 101°; $n_{\rm p}^{20}$ 1.4402) and thioanisole (10.5 g., 85%), b. p. 187 188°/759 mm.; $n_{\rm D}^{25}$ 1.5822 (lit., 25 b. p. 187–188°; $n_{\rm D}^{25}$ 1.5832). No attempt was made to isolate the small amount of dimethyl sulphide which should have been present.

A similar procedure was followed for the sulphonium salt-p-nitrobenzenethiolate reaction except that no attempt was made to isolate and characterise the olefin. The products were t-butyl methyl sulphide and p-nitrothioanisole, m. p. 71-72° (lit., 26 m. p. 71.5-72.5°).

Kinetics .-- The solvolysis of t-butyl chloride in neutral ethanol was followed by titrating for liberated acid after quenching portions in cold, dry ethanol. When ethoxide was present, reactions were followed by potentiometric titration for halide ions after quenching in dilute, alcoholic nitric acid. The previously described extraction procedure,³ followed by argentometric titration of the aqueous extract, was used for runs in which benzenethiolates were the bases. Check experiments showed that unchanged t-butyl chloride was not solvolysed during extraction.

The reactions of the sulphonium salt were followed by acid-base titration in aqueous solution (Bromothymol Blue) when alkoxides were the bases, and in alcoholic solution (Bromocresol Green) when benzenethiolates were used. In the faster reactions, a rapid mixing technique based on the use of tubes shaped in the form of an inverted Y was employed.

Olefin Proportions.-In the t-butyl chloride ethanolyses, the extraction-bromination method 27 was used. Temperatures were kept below 0° and the usual blank determinations were carried out. Olefin proportions were determined as a function of time in the neutral solvolysis so that acid-catalysed hydration of the olefin ²⁸ could be accounted for. The recorded figure is the mean of four measurements made during the first half-life of the reaction.

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In the benzenethiolate-promoted reactions of both t-butyl chloride and the sulphonium salt, titration for benzenethiol with methanolic iodine was used to estimate the extent of the elimination reaction. Olefin proportions in the former reaction were constant during a run,⁵ so that only infinity analyses were performed. In the latter reaction, olefin proportions were measured as a function of time in a few runs and were found to be constant.

However, large experimental errors were involved in determining small amounts of olefin under the concentration conditions of the sulphonium salt-benzenethiolate kinetic runs. Hence reactions of the salt (*ca.* 0.02N) and benzenethiolate (*ca.* 0.03N) in the relevant solvent containing sodium iodide (*ca.* 0.04N) were run to "infinity" at the required temperature. Analyses of benzenethiol and benzenethiolate allowed the olefin proportion to be calculated in the usual way.^{3, 18}

In all runs in which p-nitrobenzenethiolate was the base, samples were treated with an excess of methanolic iodine solution and this was followed by back-titration with a standard aqueous solution of sodium thiosulphate.

Details of a representative kinetic run are shown in Table 14.

Check Experiments.—t-Butyl methyl sulphide was stable in the presence of benzenethiolate and benzenethiol under the conditions of the kinetic experiments. t-Butyl phenyl sulphide has been shown to be likewise stable.⁵ The presence of the alkyl and alkaryl sulphides did not interfere with the iodide determination of benzenethiol in the sulphonium salt reactions.

TABLE 14

t-Butyldimethylsulphonium iodide (0.0183N) and sodium benzenethiolate (0.0587N) in ethanol at 25.0° in the presence of 0.0007M-benzenethiol. 10 ml. portions were quenched in alcoholic hydrochloric acid (0.9916N) and titrated with sodium methoxide in methanol (0.02421N) or quenched in glacial acetic acid and titrated with methanolic iodine (0.05498N)

Time (min.)	NaOMe (ml.)	I ₂ (ml.)	$10^{8}k_{2}$ (l. mole ⁻¹ sec. ⁻¹)	% Olefin $(+1.3)$
0	16.87		(()
11	18.52		6.58	
20	19.45		6.38	
27	20.44	9.33	6.58	10.1
50	21.55		6.42	
65	$22 \cdot 18$	8.65	6.43	10.3
90	22.97		6.62	
122	$23 \cdot 49$	8.12	6.56	9.8
" Infinity "	24.26	7.82	<u> </u>	10.0
,,	$24 \cdot 24$	7.82		10-0

Mean $k_2 = 6.51 \times 10^{-3}$ l. mole⁻¹ sec.⁻¹, mean olefin = 10.0%

I thank Professor B. D. England for helpful discussions and for advice in preparing this Paper. The Council of Victoria University of Wellington is thanked for the award of a Research Scholarship.

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