Employing the **A B C** classification set up in a previous paper in this series,[11] this places the bulk of the data on the borderline between the **B** and **C** regions. Comparison of these classifications for neophyl chloride and bromide in Table VI, together with those previously noted[7,9,11] for the *t*-butyl and α-phenylethyl halides, reveals a certain degree of family resemblance in the pattern of the variation of the thermodynamic quantities of activation with solvent variation.

TABLE VI

CLASSIFICATION OF THERMODYNAMIC BEHAVIOR

Solvent range	Class[a]
Neophyl chloride	
20–60% EtOH-H_2O	$60\ ^{C}\ 85\ ^{B}\ 90$
30–70% MeOH-H_2O	$60\ ^{C}\ 75\ ^{A}\ 90$
0–100% AcOH-HCOOH	$0\ ^{C}\ 35\ ^{B}\ 100$
0–50% AcOH-H_2O	$0\ ^{C}\ 35\ ^{B}\ 75$
Neophyl bromide	
20–90% EtOH-H_2O	$25\ ^{C}\ 45\ ^{B}\ 70\ ^{C}\ 88\ ^{A}\ 91$
30–90% MeOH-H_2O	$20\ ^{C}\ 85$
0–100% AcOH-HCOOH	$0\ ^{B}\ 100$
0–16 *M* H_2O in AcOH	$0\ ^{C}\ 35\ ^{B}\ 55$
20–70% dioxane-H_2O	$65\ ^{C}\ 88\ ^{B}\ 95$
50–75% Me_2CO-H_2O	$55\ ^{B}\ 80$

[a] Subscripts refer to mole percentage of fast component.

The increase in solvolysis rate arising from change of leaving group for the neophyl system from chloride to bromide is made up of an average decrease in $\Delta H^{\ddagger}$ of 1.3 ± 0.4 kcal./mole plus an average increase in $\Delta S^{\ddagger}$ of 2.4 ± 1.1 e.u. Thus, nearly 65% of the rate increase is due to decrease in the $\Delta H^{\ddagger}$ term. These results are quite similar to those previously noted for the *t*-butyl and α-phenylethyl systems.

As before,[9] a more detailed examination of these relative contributions reveals significant differences between those found for the carboxylic acid-containing solvents as opposed to the others. These comparisons are made in Table VII.

TABLE VII

CONTRIBUTION OF CHANGE IN ENTROPY AND ENTHALPY TO CHANGE IN FREE ENERGY OF ACTIVATION OF NEOPHYL BROMIDE AND CHLORIDE AT 50°

Solvent	k_{RBr}/k_{RCl}	$-T(\Delta S^{\ddagger}_{RCl} - \Delta S^{\ddagger}_{RBr})$, kcal./mole	$\Delta H^{\ddagger}_{RCl} - \Delta H^{\ddagger}_{RBr}$, kcal./mole	$\Delta F^{\ddagger}_{RCl} - \Delta F^{\ddagger}_{RBr}$ kcal./mole
EtOH-H_2O	33 ± 1	−0.8 ± 0.3	−1.4 ± 0.3	−2.2
MeOH-H_2O	34 ± 3	−1.0 ± .4	−1.4 ± .5	−2.4
Dioxane-H_2O	36 ± 4	−0.7 ± .5	−1.6 ± .4	−2.3
AcOH	13	− .3	−1.1	−1.4
HCOOH	11	− .4	−1.2	−1.6

From the data, it would appear that the reason for the low k_{RBr}/k_{RCl} ratios in the carboxylic acid-containing solvents is a combination of a decreased contribution of both the $\Delta(\Delta S^{\ddagger})$ and $\Delta(\Delta H^{\ddagger})$ terms, in approximately equal proportions.

Experimental Part

Neophyl Chloride and Bromide.—The samples employed were those previously described.[6]

Solvents.—Preparation of the solvents employed is described in detail in an earlier paper in this series.[12] In general, the solvents employed for the rate runs were from the same batches as those previously employed[12] to determine Y.

Kinetic Measurements and Experimental Results.—The techniques employed for the kinetic runs and analyses have been described previously.[12] In most cases, development of halide ion was followed. For a few of the highly aqueous alcohols and dioxanes, acidometric analysis was employed; these runs are suitably footnoted in Tables I and II. The data therein reported were based on an average of six points per run followed past 50–90% reaction. The observed kinetics were first order within experimental error for all of the solvent compositions employed except those specifically footnoted in Tables I and II. Slight upward drifts during the course of the runs were observed for neophyl bromide in acetic acid and in 60 and 70% dioxane-water. Downward drifts observed for neophyl chloride in 80% EtOH-H_2O and 80% MeOH-H_2O and for neophyl bromide in 90% MeOH-H_2O apparently were due to loss of hydrogen halide arising from secondary reaction with the solvents. For these runs, initial rate constants were estimated by linear extrapolation to zero reaction of plots of integrated rate constant *vs.* percentage reaction; these are the values listed in the tables.

LOS ANGELES 24, CALIFORNIA

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[11] A. H. Fainberg and S. Winstein (Paper IV), THIS JOURNAL, **79**, in press.

[12] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Mechanisms of Elimination Reactions. Sulfur Isotope Effects in the Decomposition of Some Sulfonium Salts

BY WILLIAM H. SAUNDERS, JR., AND SMILJKO AŠPERGER

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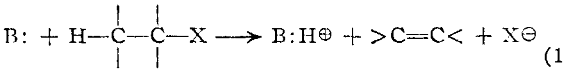
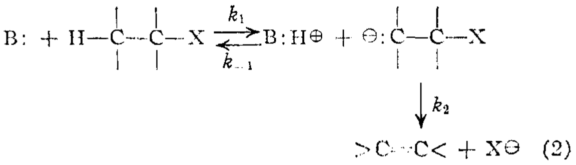
The $^{32}S/^{34}S$ isotope effect has been measured for the S_N1 decomposition of *t*-butyldimethylsulfonium iodide (I) in water and found to be *ca.* 1.8%. The E2 reaction of 2-phenylethyldimethylsulfonium bromide (II) with sodium hydroxide in water shows a much smaller isotope effect, *ca.* 0.15%. The mechanistic implications of these results are discussed.

Kinetic evidence on base-promoted elimination reactions is consistent with either a concerted process (mechanism 1) or a two-step process with a



$$\mathrm{B\!:} + \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \longrightarrow \mathrm{B\!:\!H^{\oplus}} + \mathrm{>C{=}C<} + \mathrm{X^{\ominus}} \quad (1)$$

carbanion intermediate (mechanism 2). The question of the range of applicability of these two mech-



$$\mathrm{B\!:} + \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B\!:\!H^{\oplus}} + \mathrm{{}^{\ominus}\!:\!\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \xrightarrow{k_2} \mathrm{>C{=}C<} + \mathrm{X^{\ominus}} \quad (2)$$

anisms[1] has excited considerable interest. However, efforts to establish a clear-cut case of mechanism 2 have met with little success. Eliminations from 2-phenylethyl bromide with deuteroxide ion in methanol-O-*d* and of 2-ethylbutyl bromide-2d_1 with potassium amide in liquid ammonia occur without exchange of the β-hydrogen (or deuterium).[2] Dehydrochlorination of β-benzene hexachloride with ethoxide ion in ethanol-O-*d* is accompanied by slight deuterium exchange.[3] This suggests that a carbanion intermediate, albeit of low stability, is involved in *cis* eliminations. Even when the β-hydrogen is activated by a sulfone group, there does not appear to be a carbanion intermediate of appreciable stability.[4] These experiments indicate that in most cases the intermediate carbanions, if present at all, eliminate X more rapidly than they exchange (*i.e.*, that $k_2 >> k_{-1}$ in mechanism 2).

It is also, of course, possible to envision an intermediate mechanism which is "concerted" in the sense of having no detectable intermediate, but where the transition state possesses considerable carbanion character. Evidence has been presented that the nature of the transition state in E2 eliminations may be varied rather widely by changing the leaving group, the base and the solvent.[5] In a carbanion-like transition state the C–X bond would be stretched much less than the C–H bond. There should thus be little or no isotope effect associated with the breaking of the C–X bond, for the greater part of such breaking would occur beyond the transition state.

In order to provide evidence on this point, studies were initiated of $^{32}S/^{34}S$ isotope effects in eliminations from sulfonium salts. It was first necessary to establish the magnitude of the isotope effect to be expected in the breaking of the C–S bond in a sulfonium salt. This value may be estimated from the Bigeleisen[6] theory by calculating the isotope effect for decomposition of the hypothetical C–S molecule assuming complete bond rupture in the transition state.[7] These calculations lead to isotope effects at 25° of *ca.* 1.51–1.57%, the exact figure within this range depending on the assumed value of the C–S stretching frequency.[8]

It was desirable also to establish an independent experimental value for the isotope effect. To this end, the first reaction studied was the decomposition of *t*-butyldimethylsulfonium iodide (I) in aqueous solution. This reaction follows the SN1 mechanism,[9] and it can thus be assumed that breaking of the C–S bond occurs in the rate-determining step. Once the magnitude of the isotope effect is determined, one can proceed to a similar study of typical E2 reactions of sulfonium salts and obtain a measure of the extent to which the C–S bond is weakened in the transition state. The decomposition of 2-phenylethyldimethylsulfonium bromide (II) by hydroxide ion was chosen as a suitable example. This reaction affords quantitative yields of styrene and thus interpretation of the results is not complicated by concomitant substitution.

Results

If two isotopic species (in the present case ^{32}S and ^{34}S) react at different rates, the isotopic abundance in the reactant will differ from that in the product obtained when the reaction is carried to a finite time *t*. When *t* is small, it can be shown that the ratio of rate constants for ^{32}S and ^{34}S species is given by equation 3 for the reactions under consideration, where $(^{32}S/^{34}S)_p$ is the ratio of isotopic

$$k_{32}/k_{34} = (^{32}S/^{34}S)_p/(^{32}S/^{34}S)_r \qquad (3)$$

abundances in the products and $(^{32}S/^{34}S)_r$ is the ratio of isotopic abundances in the reactants. The quantity $(^{32}S/^{34}S)_p$ was obtained by carrying the reaction to 1.5–2.0% completion, collecting the dimethyl sulfide and measuring in the mass spectrometer the ion currents at masses 62 and 64 ($Me_2{}^{32}S$ and $Me_2{}^{34}S$). The quantity $(^{32}S/^{34}S)_r$ was obtained in an analogous manner on dimethyl sulfide from complete decomposition of the sulfonium salt. The values so obtained admittedly are not absolute isotopic abundances because of small extraneous contributions to the observed ion currents such as ($^{13}CH_2{}^{32}S^{12}CH_3$) and ($^{12}CHD\text{-}{}^{32}S^{12}CH_3$) to the peak at mass 62. These contributions are difficult to assess quantitatively, but they should not affect appreciably the *ratio* of isotopic abundances which gives k_{32}/k_{34}. Since no chemical transformations are involved in this procedure, errors due to isotope fractionation in sample preparation are minimized.

The kinetics of the decomposition of I was studied at 58.95 ± 0.05° and a rate constant of 2.15 $\times 10^{-5}$ sec.$^{-1}$ obtained. This, in conjunction with the results of Hughes and Ingold,[9] allowed the calculation of the time for 2% completion as 15 min. at 58.95° and the time for 99% completion as 25 min. at 95° (actually 50 min. was allowed). After appropriate purification (see Experimental), mass spectra of the samples of dimethyl sulfide were taken over the mass range 61–65. The order of measurement was 100% sample, 2% sample, 100% sample. Each run consisted of twenty scans and the mean value of the 62/64 ratio was calculated. Standard deviation of the mean was less than 0.1% in typical measurements. The second determination on the 100% sample was made to ensure that no gross changes in instrument performance had occurred. The mean of the two 100% runs was used in calculations. Results of a series of five

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[1] These have been termed by Ingold the E2 and E1cb mechanisms, respectively; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 422.

[2] D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge and C. R. Hauser, THIS JOURNAL, **76**, 5129 (1954); P. S. Skell and C. R. Hauser, *ibid.*, **67**, 1661 (1945).

[3] S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

[4] J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3473 (1956).

[5] D. J. Cram, F. D. Greene and C. H. DePuy, *ibid.*, **78**, 790 (1956).

[6] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); J. Bigeleisen, *ibid.*, **17**, 675 (1949).

[7] W. A. Shepard and A. N. Bourns, *Can. J. Chem.*, **32**, 4 (1954), show a similar calculation for bond formation.

[8] Frequencies for sulfonium salts have not been reported. For different types of C–S bonds most values are between 700–800 cm.$^{-1}$; see C. N. Caughlan and H. V. Tartar, THIS JOURNAL, **63**, 1265 (1941); H. G. Houlton and H. V. Tartar, *ibid.*, **60**, 544 (1938).

[9] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1571 (1933); E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. McNulty, *ibid.*, 2049 (1948).

runs are recorded in Table I. The mean value of the isotope effect, 1.77%, is slightly higher than the predicted one (1.51–1.57%). However, it is not at all certain that this difference is significant. Discussion of the accuracy of the theoretical prediction is therefore of doubtful value.

TABLE I

$^{32}S/^{34}S$ ISOTOPE RATIOS AND ISOTOPE EFFECTS IN THE DECOMPOSITION OF *t*-BUTYLDIMETHYLSULFONIUM IODIDE

$^{32}S/^{34}S$ 100% completion[a]	$^{32}S/^{34}S$ 2% completion[a]	Isotope effect,[b] %
22.996	23.498	2.18
22.999		
23.129	23.566	1.71
23.210		
23.107	23.457	1.44
23.144		
23.074	23.496	1.96
23.011		
23.302	23.673	1.55
23.321		
Mean value of isotope effect		1.77[c]

[a] Ratio of the ion current at mass 62 to the ion current at mass 64. [b] % isotope effect = $(k_{32}/k_{34} - 1) \times 100$. [c] Standard deviation of the mean, 0.14; 95% confidence limit, 0.38.

The reaction of 2-phenylethyldimethylsulfonium iodide with sodium ethoxide in ethanol shows second-order kinetics and is reported to yield 89% styrene.[10] Since the reaction in aqueous solution has not been studied, we determined the kinetics of the reaction of the corresponding sulfonium bromide (II) with hydroxide ion in water at three temperatures. The results are recorded in Table II. From these results the heat of activation, $\Delta H^{\ddagger}$, is 24.8 kcal./mole and the entropy of activation, $\Delta S^{\ddagger}$, is −1.9 e.u. The proportion of styrene was measured spectrophotometrically (see Experimental). Two independent runs gave 100.7 and 99.5% styrene (mean 100.1%). Within experimental error there is thus no substitution reaction occurring.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF 2-PHENYLETHYLDIMETHYLSULFONIUM BROMIDE WITH SODIUM HYDROXIDE IN AQUEOUS SOLUTION

t, °C.[a]	$k \times 10^5$, l.-mole^{-1}-sec.$^{-1}$
40.90	1.30
58.95	11.4
70.70	43.2

[a] Temperature constant to within ±0.05°.

Isotope-effect studies on the reaction of II with hydroxide ion in water were carried out at 58.95° by a procedure analogous to that previously described for I. Table III records the results. The mean value, 0.15%, is much smaller than was found for the decomposition of I. It cannot be stated with complete confidence that the result differs significantly from zero, but it seems quite likely that the small effect is real.

TABLE III

$^{32}S/^{34}S$ ISOTOPE RATIOS AND ISOTOPE EFFECTS IN THE E2 REACTION OF 2-PHENYLETHYLDIMETHYLSULFONIUM BROMIDE WITH HYDROXIDE ION

$^{32}S/^{34}S$ 100% completion[a]	$^{32}S/^{34}S$ 2% completion[a]	Isotope effect,[b] %
23.200	23.161	+0.02
23.115		
23.046	23.015	− .10
23.030		
22.743	22.845	+ .40
22.768		
23.078	23.167	+ .29
23.124		
23.124	23.134	+ .16
23.070		
Mean value of isotope effect		+ .15[c]

[a,b] See corresponding footnotes in Table I. [c] Standard deviation of the mean, 0.09; 95% confidence limit, 0.25.

Discussion

Since most reactions that produce carbonium ions appear to have transition states closely resembling the carbonium ion,[11] it seems reasonable to assume that the isotope effect for the hydrolysis of I is a good approximation to the maximum isotope effect for C–S bond cleavage. In sharp contrast to this is the very small isotope effect in the E2 reaction of II. One may then conclude that the C–S bond of II is stretched very little in the transition state. It therefore appears that the transition state for the elimination possesses considerable carbanion character. We cannot say from our evidence whether the reaction follows the two-step carbanion mechanism, but it seems rather unlikely that a carbanion of appreciable stability is involved. Experiments aimed at elucidating this question have been undertaken.[12]

It has been suggested that the transition state for E2 eliminations probably resembles reactants more closely than products.[13] If this is true, neither the C–H nor the C–S bond would be stretched very much and a small sulfur isotope effect might still be consistent with synchronous loss of the elements of hydrogen and dimethyl sulfide. We do not favor this explanation for several reasons. First, eliminations from substituted 2-phenylethyldimethylsulfonium salts are accelerated by electron-withdrawing and hindered by electron-repelling substituents.[14] Second, examples of substantial deuterium[15] and tritium[16] isotope effects have been noted in E2 reactions of isopropyl bromide and 2-(*p*-nitrophenyl)-ethyltrimethylammonium iodide, respectively. While results on sulfonium salts are not yet available, it seems reasonable to expect that a sizable hydrogen isotope effect will be found here also.

The applicability of the present conclusions to E2 reactions of simple alkylsulfonium salts is not entirely clear. Undoubtedly the phenyl group

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(10) E. Hughes, C. Ingold and G. Maw, *J. Chem. Soc.*, 2072 (1948).

(11) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(12) The conventional approach using a deuterated solvent to study deuterium exchange would be useless in the present case, since the α- and methyl hydrogens would probably exchange faster than the elimination occurs; see W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

(13) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956).

(14) R. A. Williams, unpublished results in these laboratories.

(15) V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

(16) E. M. Hodnett and J. J. Flynn, Jr., Abstracts of Papers, 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 16–21, 1956.

effects a considerable stabilization of a carbanion-like transition state through delocalization of the negative charge, but it should also stabilize the incipient double bond of the synchronous mechanism. Probably the carbanion character of the transition state is less pronounced with simple sulfonium salts. It seems likely, however, that it is still appreciable.[17]

Acknowledgments—We wish to thank Mr. C. A. Whiteman for advice and assistance on the use of the mass spectrometer. The mass spectrometer was purchased with the aid of grants from E. I. du Pont de Nemours and Co. and the Esso Education Foundation. We also thank Professor A. N. Bourns for helpful discussions.

Experimental[18]

_t_-Butyldimethylsulfonium Iodide.—Equimolar quantities of _t_-butyl iodide and dimethyl sulfide were mixed in nitromethane.[9] After three days the crystalline product was separated and recrystallized from methanol. It decomposed at _ca._ 150° (lit.[9] 160°). The decomposition point is unreliable as a criterion of purity, being quite sensitive to the rate of heating, so the purity was verified by analysis. _Anal._ Calcd. for $C_6H_{15}SI$: C, 29.27; H, 6.14; I, 51.56. Found: C, 29.01; H, 5.96; I, 51.56.

2-Phenylethyldimethylsulfonium Bromide.—Equimolar quantities of methyl 2-phenylethyl sulfide[19] and methyl bromide were mixed in nitromethane. After recrystallization from ethanol–ether, the product decomposed at 135.5°. _Anal._ Calcd. for $C_{10}H_{15}SBr$: C, 48.58; H, 6.12; Br, 32.15. Found: C, 48.74; H, 6.28; Br, 32.15.

Preparation of Samples for Measurement of Mass Spectra. 1. **Samples from _t_-Butyldimethylsulfonium Iodide.**—(a) **100% Completion.**—The sulfonium iodide (0.20 g.) was dissolved in 200 ml. of water in a gas-washing bottle. To the outlet of the bottle was attached a small condenser (to hold back most of the water vapor), followed by a trap cooled with liquid nitrogen. The bottle was immersed in a water-bath held at 95°. A stream of nitrogen, purified by passage through Ascarite and a Dry Ice trap, was bubbled slowly through the solution to expel the dimethyl sulfide. After 50 min. (>99% completion of reaction) the trap was set aside (still immersed in liquid nitrogen).

(b) **2% Completion.**—The sulfonium iodide (5.9 g.) was quickly added to 200 ml. of water in the apparatus described above. The water previously had been equilibrated to 58.95° in the thermostat. The reaction mixture was held at 58.95° for 15 min. The reaction vessel was transferred to an ice–water bath to stop the reaction, and the bubbling of nitrogen was continued for another 10 minutes to expel the remaining dimethyl sulfide. The dimethyl sulfide was collected as in I(a).

2. **Samples from 2-Phenylethyldimethylsulfonium Bromide.** (a) **100% Completion.**—A 25-ml. portion of an aqueous solution 0.1 _M_ in the sulfonium bromide and 0.2 _M_ in sodium hydroxide was heated at 97° for 150 min. and the dimethyl sulfide collected as in 1 (a).

(b) **2% Completion.**—To 275 ml. of 0.2 _M_ sodium hydroxide, previously equilibrated to 58.95°, was added 0.0275 mole of the sulfonium bromide. After 15 min. the reaction was stopped by cooling and the bubbling of nitrogen continued for another 10 minutes as before (1 (b)).

Purification of Dimethyl Sulfide Samples.—The trap containing dimethyl sulfide, still immersed in liquid nitrogen, was attached to a vacuum line through a tube which contained phosphorus pentoxide. The stopcock to the line was opened and the trap pumped briefly to remove any liquid oxygen. The stopcock was closed, the liquid nitrogen removed and the trap allowed to warm until its contents collected at the bottom. The trap was again immersed in liquid nitrogen and the system evacuated to a few microns. Pumping was discontinued and the liquid nitrogen bath transferred to a sample tube of 50-ml. capacity which previously had been attached to the line. The dimethyl sulfide was thus transferred to the sample tube, and water vapor was retained in the phosphorus pentoxide. The drying tube and trap were now removed from the line. The dimethyl sulfide was degassed by evaporation and refreezing followed by evacuation to <1 μ. This process was repeated two times. Care was taken to apply exactly the same procedure to the 100% and 2% sample in each run.

Mass Spectrometry.—A Consolidated model 21-620 recording mass spectrometer was used for all measurements. The same sample pressure (_ca._ 500 μ) was used for all samples to cancel any possible error in the zero line. Peak heights were kept roughly constant at nearly full-scale deflection by this procedure. Samples were measured in the order described under Results. Attenuator settings for masses 62 and 64, respectively, were kept constant from run to run. Complete mass spectra of selected samples were determined and compared with the mass spectrum of pure dimethyl sulfide. Samples from _t_-butyldimethylsulfonium iodide showed a few extraneous peaks well below the 62–64 mass range (isobutylene ?) but none in or above this range. Samples from 2-phenylethyldimethylsulfonium bromide showed no extraneous peaks over the entire range.

Kinetic Measurements.—The kinetics of the decomposition of _t_-butyldimethylsulfonium iodide in 0.1 _M_ aqueous solution was followed by titration of chilled aliquots of the reaction mixture with standard sodium hydroxide. The kinetics of the reaction of 2-phenylethyldimethylsulfonium bromide (0.1 _M_) with sodium hydroxide (0.1 _M_) in water was followed by the addition of aliquots to cold 0.1 _M_ hydrochloric acid and back-titration with 0.1 _M_ sodium hydroxide. The thermostat held within ±0.05° of the stated temperature. Average deviations of the reported rate constants are 1–2%.

Olefin Analysis.—An aqueous solution 0.1 _M_ in 2-phenylethyldimethylsulfonium bromide and 0.2 _M_ in sodium hydroxide was heated on the steam-bath for 5 hr. The mixture was diluted by a factor of 5000 with absolute ethanol and the styrene absorption measured at 248 mμ on a Beckman DU spectrophotometer. The molar extinction coefficient at this wave length for freshly distilled styrene in ethanol was 1.35×10^4. Two runs gave 100.7 and 99.5% styrene. Measurements were made at a concentration of _ca._ 2×10^{-5} _M_. It was established that the sulfonium salt, dimethyl sulfide, sodium bromide and sodium hydroxide show no observable absorption at this level of concentration.

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(17) A referee has asked us to comment on the relation between our results and those of Cram.[5] The evidence given by Cram indicates that 1,2-diphenyl-1-propyltrimethylammonium iodide reacts with ethoxide ion in ethanol _via_ a transition state possessing considerable double-bond character. We feel that the major factor here lies in the different structure of the alkyl moiety. Cram's system possesses an α-phenyl group which should encourage the heterolysis of the C–N bond and stabilize a developing double bond. Similarly, the β-methyl group should render more difficult the heterolysis of the C–H bond. Both of these factors would lead to greater "concertedness" of the reaction. Thus our results are not necessarily inconsistent with the generally similar behavior of sulfonium and ammonium salts in elimination reactions. The referee suggests that some special property of sulfonium salts, such as the ability of sulfur to expand its octet, may be responsible for the difference. This possibility cannot be excluded, but in the absence of decisive evidence we prefer the above explanation.

(18) Melting points are corrected. Carbon and hydrogen analyses by Miss A. Smith.

(19) Prepared by the procedure of E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 92 (1949).