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# Alkaline Decomposition of Triarylsulfonium Halides with Various Bases[1]

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Alkaline decomposition of triarylsulfonium bromides with various bases was found to give different products depending on the nature of the bases. The reaction of triarylsulfonium bromide with either piperidide anion or thiophenoxide ion seems to proceed with the initial attack of piperidide anion or thiophenoxide ion of the carbon atom of C–S bond ($S_N$ reaction on carbon atom), while the reaction of diarylethoxysulfonium tetrafluoroborate with thiophenoxide ion is presumed to involve the initial attack of thiophenoxide ion on the sulfur atom at low temperature ($S_N$ reaction on sulfur atom). When triarylsulfonium bromide was subjected to the reaction with potassium hydroxide in aqueous ethanol, the main path was the alkaline decomposition which proceeds *via* the nucleophilic attack of the ethoxide ion on the sulfur atom. In the treatment with hydroxide ion in water, the decomposition appears to proceed mainly *via* two mechanistic routes, *i.e.*, the processes involving the nucleophilic attack of hydroxide ion on both aromatic carbon and the sulfur atoms. A free radical process cannot be excluded, but appears unlikely.

In a previous work,[2] it was found that the alkaline decomposition reaction is presumably initiated by the attack of ethoxide ion on the sulfur atom of the sulfonium salts occured competitively along with $S_N$ reaction of aromatic chloride.

In view of the formation of the various products in the treatment of triarylsulfonium salts with bases, the alkaline decompositions of triarylsulfonium salts seem to proceed *via* different routes depending on the nature of the bases. Namely, one portion undergoes a cleavage reaction *via* the initial attack on the sulfur atom ($S_N$ reaction on sulfur atom), another involves a reaction *via* the attack on the aromatic carbon atom of C–S bond ($S_N$

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[1] Paper III on Sulfonium Salt. Paper II, Y. H. Khim and S. Oae, This Bulletin, **42**, 1968 (1969).

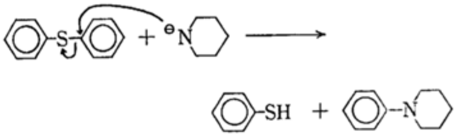
[2] S. Oae and Y. H. Khim, *ibid.*, **42**, 1622 (1969).

reaction on carbon atom), and another proceeds through the initial removal of a proton to the sulfonio group followed by the subsequent elimination of sulfide group to form "benzyne" intermediate. In order to clarify the nature of the modes of alkaline decomposition of triarylsolfonium halides with various bases, the reactions of triarylsulfonium salts with piperidide anion, sodium arylthiolate, ethoxide and hydroxide ion have been carried out in various solvents. The details of alkaline decomposition and the mechanistic interpretation are presented in this paper.

**Reaction of Triphenyl- and Tri-*p*-tolyl-sulfonium Bromides with Potassium Amide in Piperidine.** When triphenylsulfonium bromide was reacted with potassium hydroxide in boiling piperidine under the conditions shown in Table 1, diphenyl sulfide, thiophenol and *N*-phenylpeperidine were obtained quantitatively.

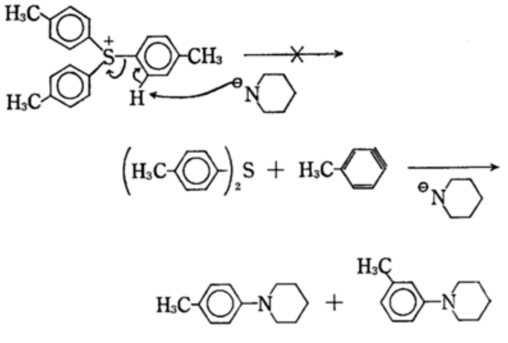
From analyses of the products, the alkaline cleavage reaction seems to proceed with the initial attack of piperidide anion on the carbon atom of C–S bond bearing sulfide group, while diphenyl sulfide formed reacts further with piperidide anion to give thiophenol and *N*-phenylpiperidine.

It has been suggested[3] that the cleavage reaction of diphenyl sulfide with sodium amide in boiling piperidine proceeds through the initial attack of peperidide anion on the carbon atom of diphenyl sulfide as follows.



(1)

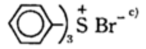
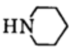
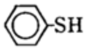
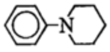
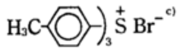
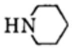
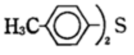
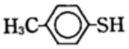
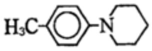
However, since this particular reaction is performed between a positively charged species *i.e.* sulfonium salt and a very strong base in a heterogeneous system, there remains a possibility that the reaction proceeds through the initial abstraction of *o*-hydrogen followed by the subsequent elimination of sulfide group to form "benzyne" intermediate, to which piperidide anion adds to result in the final product as shown below.



(2)

In order to examine the "benzyne" mechanism tri-*p*-tolylsulfonium bromide was subjected to the alkaline decomposition reaction, since this mechanism requires the formation of both *meta*- and *para*-substituted *N*-*p*-tolylpiperidines. Identification of both *meta*- and *para*-*N*-tolylpiperidines can be easily performed by the comparison of their characteristic infrared absorption bands (*m*-derivative 10.5, 12.95 $\mu$; *p*-derivative 12.32 $\mu$) and also by gas chromatography. When the reaction was actually carried out under the conditions shown in Table 1, only the *para*-substituted compound was obtained, but

Table 1. The alkaline decomposition of triarylsulfonium bromide with potassium amide in piperidine

| Sulfonium salts | Solvent | Base | Temp. (°C) | Time (hr) | Products | Yield (%) |
|---|---|---|---|---|---|---|
|  |  | $KNH_2$[c] | 106 | 5 | Ph–S–Ph (50) | 92[a] |
| | | | | |  (42) | |
| | | | | |  | 90[b] |
|  |  | $KNH_2$[c] | 106 | 5 |  | 85 |
| | | | | |  | |
| | | | | |  | 80 |

a) The yield is a combined percentage of sulfide and thiophenol.
b) The yield was obtained based on the molar concentration of starting sulfonium salt.
c) The molar ratio of sulfonium and potassium amide was 1 : 4.

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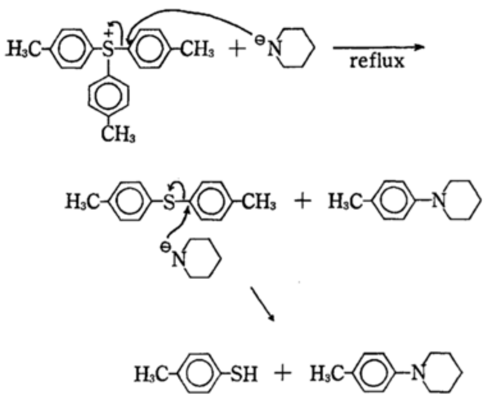
[3] a) W. E. Truce, D. P. Tate and D. N. Burge, *J. Am. Chem. Soc.*, **82**, 2872 (1960). b) R. Otto, *Ber.*, **19**, 2425 (1886). c) S. Oae and R. Kiritani, This Bulletin, **38**, 765 (1965). d) N. Furukawa, H. Tanaka and S. Oae, *ibid.*, **41**, 1463 (1968).

no *meta-N*-tolylpiperidine.

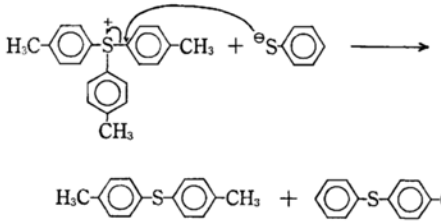
Thus the most plausible route for this reaction may be the one involving the aromatic $S_N2$ process.



(3)

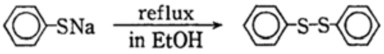
**Reaction of Triarylsulfonium Bromide and Ethoxy-diphenyl-sulfonium Tetrafluoroborate with Sodium Arylthiolate in Ethanol.** Triarylsulfonium bromides were subjected to the alkaline decomposition with sodium arylthiolate in ethanol and the detailed analyses of the products formed in the reaction were undertaken in order to choose possible mechanistic pathways for the reaction. The solution of tri-*p*-tolylsulfonium bromide and sodium thiophenoxide in ethanol was gently refluxed in ethanol under the conditions given in Table 2. The products isolated were found to contain di-*p*-tolyl sulfide and phenyl-*p*-tolyl sulfide as the main products and a small amount of diphenyl disulfide as the minor product. The products and yields for other similar reactions are shown in Table 2. Identification and determination of the yields of products obtained were performed by means of quantitative vapor phase chromatography and by comparison of their infrared spectra with those of the authentic samples.

From the distribution of the whole products and their yields, the reaction (runs 1—4) seems to proceed *via* the nucleophilic attack on the carbon atom of C-S bond similarly to the case of the reaction of triarylsulfonium bromide with piperidide anion (Eq. (4)).



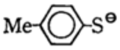
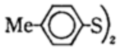
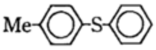
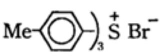
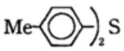
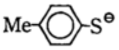
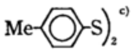
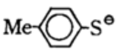
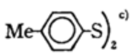
(4)

The formation of a small amount of diaryl disulfide (runs 1—4) undoubtedly results from the oxidation of sodium arylthiolate itself in boiling ethanol (Eq. (5)), because the yields of diaryl disulfides do not differ much regardless of the absence or presence of the sulfonium salts in the reaction system (run 3), and the yield of diphenyl disulfide in the



(5)

Table 2. The reaction of sulfonium salts with sodium arylthiolates in ethanol

| Run | Sulfonium salt | Base | Sulfonium : Base | Temp. (°C) | Time (hr) | Products (Yield %) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Sulfides | Disulfides |
| 1 | $(\mathrm{Ph-})_3\overset{+}{\mathrm{S}}\ \mathrm{Br}^-$ | $\mathrm{Ph-S}^{\ominus}$ | 1 : 3 | 78 | 4 | $(\mathrm{Ph-})_2\mathrm{S}$ (180)[a] | $\mathrm{Ph-S})_2$ (7) |
| 2 | $(\mathrm{Ph-})_3\overset{+}{\mathrm{S}}\ \mathrm{Br}^-$ |  | 1 : 3 | 78 | 4 | $(\mathrm{Ph-})_2\mathrm{S}$ (90) |  (8) |
| | | | | | |  (80) | |
| 3 | —— | $\mathrm{Ph-S}^{\ominus}$ | — | 78 | 4 | —— | $\mathrm{Ph-S})_2$ (5)[b] |
| 4 |  | $\mathrm{Ph-S}^{\ominus}$ | 1 : 1 | 78 | 6 |  (90) | $\mathrm{Ph-S})_2$ (small) |
| 5 | $\left[(\mathrm{Ph-})_2\overset{+}{\mathrm{S}}\mathrm{-OEt}\right]\ \mathrm{BF}_4^-$ |  | 1 : 1 | −5—−10 | 1.5 | $(\mathrm{Ph-})_2\mathrm{S}$ (42)[c] | [c] (40) |
| 6 | 〃 |  | 1 : 2 | −5 | 1 | $(\mathrm{Ph-})_2\mathrm{S}$ (90)[c] | [c] (80) |

a) The apparent yield is based on moles of sulfonium salt; the real yield from the cleavage reaction is 90%.

b) Without sulfonium salt, sodium thiophenoxide itself upon being acidified in the air gave diphenyl in ethanol.

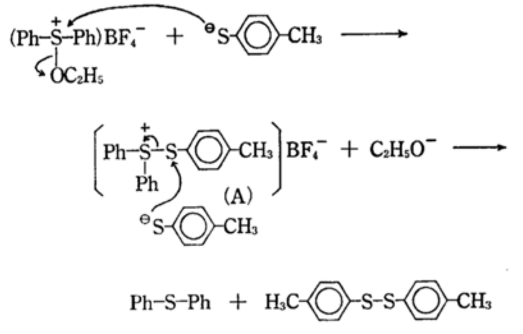
c) The moles of both diphenyl sulfide and ditolyl disulfide are almost same.

reaction with equimolar mixture of tri-*p*-tolylsulfonium bromide and sodium thiophenoxide (run 4) is much smaller than that in the case with a mixture in which the ratio of sodium thiophenoxide over sulfonium salt is three.

Another possible mechanism of $S_N$ reaction on sulfur atom of triarylsulfonium salt may be considered. If the reaction proceeds *via* $S_N$ reaction at sulfur atom, it should give toluene or benzene as in the case of the reaction of triarylsulfonium halide with phenyllithium, where the nucleophilic attack of phenyl anion on sulfur atom of sulfonium salt was actually detected.[4]

In no case, however, could the formation of any hydrocarbon be detected. Therefore, the $S_N$ reaction on the sulfur atom can be ruled out.

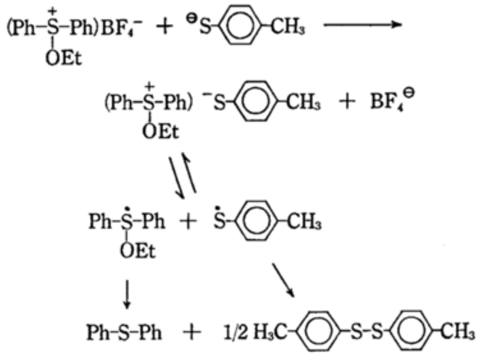
When diphenylethoxysulfonium tetrafluoroborate was subjected to the reaction with sodium *p*-toluenethiolate under the conditions shown in Table 2 (run 5, 6), the products isolated from the reaction were both diphenyl sulfide and ditolyl disulfide. From the products the reaction seems to proceed first *via* the attack of the nucleophile on the sulfur atom of the sulfonium salt with ethoxy group as the leaving group, involving the initial formation of an unstable *p*-tolylthiodiphenylsulfonium ion intermediate (A). It then seems to proceed through the attack of the same nucleophile on the S atom of *p*-tolylthio group of the intermediate sulfonium ion, with diphenyl sulfide as the leaving group as shown below.



(6)

Since the ethoxy group is a better leaving group than the diphenyl sulfide group, *p*-toluenethiolate ion may easily attack the sulfur atom in contrast to the aromatic substitution of tri-*p*-tolylsulfonium bromide with thiophenoxide ion in which diphenyl sulfide is the leaving group. The problem of attacking site of nucleophilic reagent in the $S_N$ reaction of sulfonium salt can easily be explained by the relative ease and stability of the leaving group. Recently, Kice and his co-workers[5] have revealed that the scission of the sulfur-sulfur bond of aryl-hydroxy-arylthio-sulfonium ion in the reaction of aryl arylthiolsulfinate with nucleophilic reagents occurs at the sulfur atom of arylthio group, but not at the sulfur of aryl-hydroxysulfonio ion. Recently McEwen and Knapcyzyk[6] suggested that the reaction of triarylsulfonium halides with alkoxide ion in alcohol solbents proceeds *via* a radical process.

If the reaction of diphenyl-ethoxysulfonium bromide with *p*-toluenethiolate ion involves a radical process in which the electron transfer occurs, as in Eq. (7), the reaction between equimolar amounts of the sulfonium and *p*-toluenethiolate ion should give a mixture of an equimolar amount of diphenyl sulfide and a half molar amount of di-*p*-tolyl disulfide, while in the case of the usual $S_N$ reaction on the sulfur atom, the decomposition of the sulfonium salt is expected to give equimolar mixture of both diphenyl sulfide and di-*p*-tolyl disulfide.



(7)

The results shown in runs 5 and 6 in Table 2, reveal that almost the same molar quantities of both sulfide and the disulfide were obtained. Therefore, the alkaline decomposition of the diaryl-ethoxysulfonium tetrafluoroborate with *p*-toluenethiolate ion in ethanol is presumed to proceed through the initial nucleophilic attack of the arylthiolate anion on the sulfur atom of the sulfonium compound.

**Reaction of Triarylsulfonium Bromide with Potassium Hydroxide in Aqueous Ethanol and Water.** The reaction of a triarylsulfonium bromide with potassium hydroxide in aqueous ethanol gave corresponding diaryl sulfide, hydrocarbon and resins as the main products and a small amount of ethyl aryl ether. A similar decomposition of the sulfonium salt in water under prolonged heating conditions at higher tempera-

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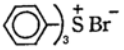
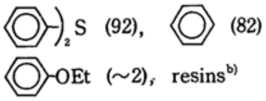
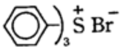
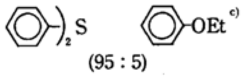
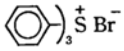
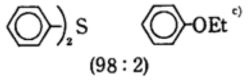
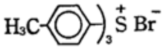
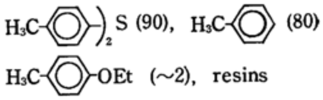
[4] a) V. Franzen and C. Mertz, *Ann.*, **643**, 24 (1961). b) Y. H. Khim and S. Oae, This Bulletin, **42**, 1968 (1969).

[5] a) J. L. Kice and E. H. Markved, *J. Am. Chem. Soc.*, **86**, 2270 (1964). b) J. L. Kice and G. Guaraldi, *ibid.*, **88**, 5236 (1966). c) J. L. Kice, C. G. Venier and L. Heasley, *ibid.*, **89**, 3557 (1967).

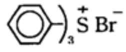
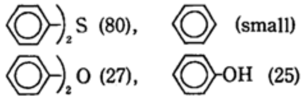
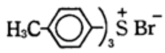
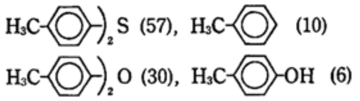
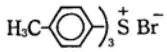
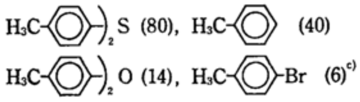
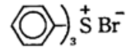
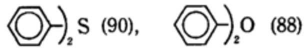
[6] J. W. Knapczyk, G. H. Wiegand and W. E. McEwen, *Tetrahedron Letters*, **1965**, 2971.

TABLE 3. THE REACTION OF TRIARYLSULFONIUM BROMIDE WITH POTASSIUM HYDROXIDE IN AQUEOUS ETHANOL[a]

| Sulfonium | Solvent molar ratio $C_2H_5OH : H_2O$ | Base | Temp. (°C) | Time (hr) | Products (yield %) or molar ratio |
|---|---|---|---|---|---|
|  | 44 : 56 | KOH | 105 | 7 |  S (92), (82)<br>OEt (~2), resins[b] |
|  | 97 : 3 | KOH | 105 | 7 |  S OEt[c]<br>(95 : 5) |
|  | 1.77 : 98 | KOH | 120 | 24 |  S OEt[c]<br>(98 : 2) |
|  | 44 : 56 | KOH | 105 | 10 |  S (90), (80)<br>OEt (~2), resins |

a) The reaction was carried out in an ampoul.
b) Perhaps, acetaldehyde is polymerized to give aldol resins.
c) The molar ratio of diphenyl sulfide and phenetole was determined by using quantitative vapor phase chromatography. Besides these products, benzene and resins were also confirmed.

TABLE 4. THE REACTION OF TRIARYLSULFONIUM BROMIDE WITH POTASSIUM HYDROXIDE IN WATER[a]

| Sulfonium[b] salt | Solvent | Base[b] | Temp. (°C) | Time (hr) | Products (yield %) |
|---|---|---|---|---|---|
|  | $H_2O$ | KOH | 150—160 | 50 |  S (80), (small)<br>O (27), OH (25) |
|  | $H_2O$ | KOH | 150—160 | 150 |  S (57), (10)<br>O (30), OH (6) |
|  | $H_2O$ | KOH | 210—230 | 100 |  S (80), (40)<br>O (14), Br (6)[c] |
|  | $H_2O$ | KOH<br>Ph-OH | 160—180 | 50 |  S (90), O (88) |

a) The reaction was carried out in an ampoul.
b) The molar ratio of starting sulfonium salt and potassium hydroxide is 1 : 8.
c) The formation of *p*-tolyl bromide could be explained in terms of the intramolecular decomposition. McEwen and Wiegand[7] demonstrated that triarylsulfonium halides might proceed *via* an intramolecular decomposition at 250°C to give sulfides and aryl halides.
d) The molar ratio of starting salt: KOH : phenol is 1 : 8 : 4.

ture as shown in Table 4 yielded the diaryl sulfide, the diaryl ether, phenol, and hydrocarbon compounds.

The results and the experimental conditions are tabulated in Tables 3 and 4. There is a big difference in the products and their yields between the alkaline decompositions of the triarylsulfonium salt in aqueous ethanol and that in water, although experimental conditions also somewhat differ from each other.

Considering the main products of sulfide, hydrocarbon compound and resins obtained from the reaction in aqueous ethanol, the decomposition of triarylsulfonium bromide with ethoxide ion seems to proceed mainly through the initial attack of the ethoxide ion on the sulfur atom of the sulfonium salt and the rest, through the process shown below.

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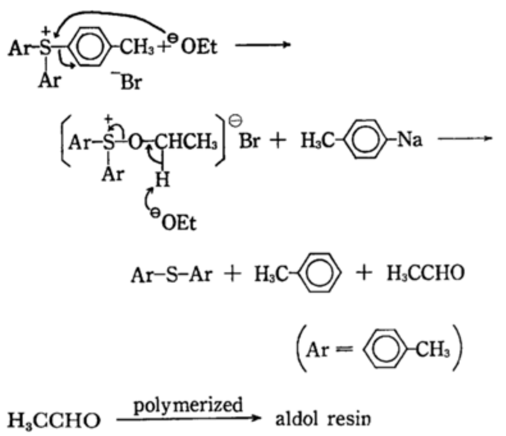
[7] G. H. Wiegand and W. E. McEwen, Tetrahedron Letters **1965**, 2639; *J. Org. Chem.*, **33**, 2671 (1968).



(8)

Since both hydroxide and ethoxide ions can exist in an equilibrium in aqueous ethanol, one could expect that the hydroxide ion should participate in the alkaline decomposition if the amount of water increases. From the products analyses of the reaction of the triphenylsulfonium bromide with potassium hydroxide from 1.6 to 97 mol % aqueous ethanol, the reaction seems to proceed mainly through the nucleophilic attack of only ethoxide ion on the sulfur atom of the sulfonium salt.

In a previous paper,[2] it was revealed that the alkaline decomposition of the triarylsulfonium bromide with ethoxide ion in 70% (vol%) aqueous ethanol obeys the second order kinetic rate low; first order with respect to both the sulfonium and potassium hydroxide concentrations.

Thus, the kinetic experiment of the alkaline decomposition was carried out in order to examine the solvent effect of various water and ethanol mixtures. The values of the rate constants for the alkaline decompositions in various aqueous ethanol solvents at 120°C are shown in Table 5. Figure 1 records a plot of the mol per cent of ethyl alcohol in water against the log of second order rate constant. The results indicate that the rate of the decomposition is increased about $10^6$ fold by increasing the ethanol concentration (97.7 mol%) from 98.33 mol % of water.

TABLE 5. THE RATES OF ALKALINE DECOMPOSITION OF TRIPHENYLSULFONIUM BROMIDE WITH ETHOXIDE ION IN AQUEOUS ETHANOL AT 120±0.1°C

| Solvent ($H_2O$-$C_2H_5OH$) W% $C_2H_5OH$ | Mol% $C_2H_5OH$ | $k_2$ $mol^{-1}\,l\,sec^{-1}$ |
|---|---|---|
| | 0.96 | ——a) |
| 6.25 | 1.77 | $2.90\times10^{-6}$ |
| 38.00 | 16.00 | $7.80\times10^{-5}$ |
| 46.50 | 26.80 | $2.95\times10^{-4}$ |
| 61.00 | 40.00 | $5.73\times10^{-4}$ |
| 81.00 | 63.50 | $1.39\times10^{-3}$ |
| 90.00 | 80.00 | $5.34\times10^{-3}$ |
| 97.00 | 93.00 | $2.38\times10^{-1}$ |
| 98.00 | 95.30 | $7.60\times10^{-1}$ |
| 99.00 | 97.70 | $9.32\times10^{-1}$ |

a) After the reaction mixture was heated for 48 hr, the starting sulfonium bromide was recovered almost quantitatively.

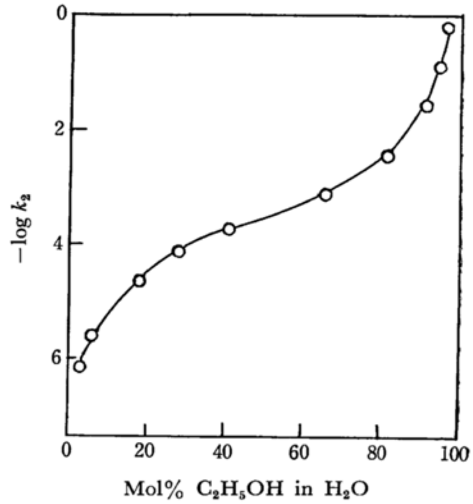
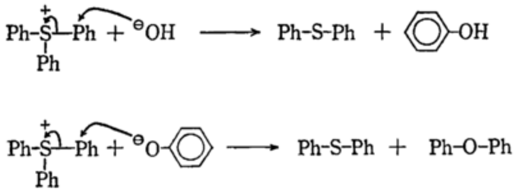


Fig. 1. Plot of mole percentage of ethyl alcohol in water against negative logarithm of $k_2$ ($mol^{-1}\,l\cdot sec^{-1}$) for the reaction of triphenylsulfonium bromide with potassium hydroxide.

The curve in Fig. 1 is of a shape observed frequently in the solvent effect of the reaction in the reactions of the mixted solvents. Although the plot is almost linear from 30 to 80 mol % of ethyl alcohol the rates rise much more steeply at lower and higher concentrations. In the case of pure water, after the reaction mixture was heated at 120°C for 50 hr, the starting solfonium salt was quantitatively recovered. From the results obtained in the kinetic experiments, it may be concluded that ethoxide ion which is more nucleophilic than hydroxide ion attacks preferentially the sulfonium ion undergoing alkaline decomposition.

$$HO^{\ominus}\cdots HOH + HOC_2H_5 \rightleftarrows HO^{\ominus}\cdots HOC_2H_5$$
$$\leftrightarrows {}^{\ominus}OC_2H_5 + H_2O$$

When the triphenylsulfonium bromide was subjected to reaction with potassium hydroxide in water under severer conditions as shown in Table 4, the isolated compounds were diphenyl sulfide (87 %), diphenyl ether (27 %), phenol (25 %) and a small amount of benzene in contrast to the case of the similar reaction in aqueous ethanol. From the distribution of the products, the decomposition of triphenylsulfonium bromide with potassium hydroxide in water seems to involve the initial attack of hydroxide ion on the carbon atom of C–S bond to form phenolate ion, which in turn



attacks the carbon atom of the sulfonium salt yeilding diphenyl ether. Phenoxide ion may be more nucleophilic than hydroxide ion. In the presence of phenoxide ion, the alkaline decomposition of triphenylsulfonium bromide gave an equimolar mixture of both diphenyl sulfide and diphenyl ether quantitatively under the same condition as shown in Table 4.

Another possible mechanism of benzyne route is considered, because diphenyl sulfide, phenyl ether and phenol can be formed by the abstraction of *o*-hydrogen followed by the elimination of sulfide group to form benzyne intermediate.

Benzyne has been postulated as being an intermediate between the triarylsulfonium halides and a base in other reactions.[4] In order to examine the benzyne mechanism, tri-*p*-tolylsulfonium bromide was subjected to the reaction with hydroxide ion in water under the condition shown in Table 4, since this mechanism requires the formation of both *meta*- and *para*-ditolyl ether.

The compound isolated is only the *para* substituted compound *p,p'*-ditolyl ether, whose identification can be easily performed by the comparison of its characteristic IR.

Therefore, the possibility of the benzyne precess is ruled out.

It is noteworthy that the decomposition of triphenylsulfonium bromide with hydroxide ion in water gives a small amount of benzene whereas a similar reaction of tri-*p*-tolylsulfonium bromide with hydroxide ion affords a higher yield of toluene than that of benzene, especially at higher reaction temperature, though the experimental conditions are somewhat different. The reaction system of triphenylsulfonium salt is homogeneous, while that of tri-*p*-tolylsulfonium salt is heterogeneous and so requires a higher reaction temperature and longer time as shown in Table 4.

In the case of the alkaline decomposition of tritolylsulfonium bromide, the yield of toluene increases with the rise of reaction temperature and that of *p*-cresol and its derivatives decreases. It could be that in the case of tri-*p*-tolylsulfonium salt the heterogeneous reaction system and higher reaction temperature are preferable for a radical process.

It could be garued that the diaryl sulfide, diaryl ehter, phenol and hydrocarbon compounds also arise through a radical process[6] although it is not very likely.

The formation of phenol in this reaction could be explained by the following equations.

$$\mathrm{Ar_3\overset{+}{S}\overset{-}{Br}} + {}^{\ominus}\mathrm{OH} \rightarrow \mathrm{Ar_3\overset{+}{S}\overset{-}{OH}} + \mathrm{Br}^{\ominus} \rightleftarrows \mathrm{Ar_3SOH}$$

$$\rightleftarrows [\mathrm{Ar_3\dot{S}\ \dot{O}H}] \rightarrow \mathrm{Ar_2S} + \mathrm{ArOH} \qquad (9)$$

If the phenoxide ion formed by the dissociation of phenol obtained in the radical process would again attack the carbon atom of the C–S bond ($S_N$ reaction on a carbon atom) analogous to hydroxide ion, diaryl ether should be obtained.

When the decomposition of a triarylsulfonium salts took place both in the presence and absence of oxygen, the ratio of all the phenol derivatives to diaryl sulfide produced did not differ. In the case of a radical process, a higher yield of phenol and phenol derivatives in the presence of oxygen than that in the absence of oxygen can be expected. However, at the present time a definite conclusion to these complicating reactions of the triarylsulfonium bromide with hydroxide ion in water can not be drawn.

## Experimental

**Triphenyl- and Tri-*p*-tolylsulfonium Bromide.** The titled triarylsulfonium bormides were prepared from diarylethoxysulfonium tetrafluoroborate and aryl Grignard reagent according to the usual methods.[2]

**The Reaction of Triphenylsulfonium Bromide with Potassium Amine in Piperidine.** Sodium amide (0.5 g, 0.012 mol) which was washed with anhydrous *n*-hexane before use, was refluxed in piperidine (10 m*l*) for 30 min. To this solution was added triphenylsulfonium bromide (1 g, 0.003 mol) and the mixture was refluxed for about 5 hr. After cooling, the solution was quenched with ice water to decompose sodium amide. The aqueous solution was extracted with ether; the aqueous layer was carefully acidified with 1 N hydrochloric acid and extracted again with ether. After evaporation of ether, thiophenol (40 %) was obtained. The first ether layer was distilled and the distillate fractionated by vapor phase chromatography. Identification and determination of the yields of the products were performed using quantitative vapor phase chromatography and by comparison of their infrared spectra with those of authentic samples. The isolated compounds from the organic layer are diphenyl sulfide (50 %) and *N*-phenylpiperidine (90 %). The reaction of tri-*p*-tolylsulfonium bromide with potassium amide in piperidine was carried out similarly to that of triphenylsulfonium salt. The results are shown in Table 1.

**The Reaction of Tri-*p*-tolylsulfonium with Sodium Thiophenoxide.** Tri-*p*-tolylsulfonium bromide (2 g, 0.0026 mol) was dissolved in ethanol (30 m*l*). To this solution was added sodium thiophenoxide (2.08 g, 0.0104 mol) in ethanol (20 m*l*) with stirring. After the reaction mixture was refluxed for 4 hr, it was poured into ice water and acidified with dilute hydrochloric acid, extracted with ether, washed, dried over magnesium sulfate. The compounds isolated from the organic layer were di-*p*-tolyl sulfide (92 %) and phenyl *p*-tolyl sulfide (90 %) and a small amount of diphenyl disulfide. The purity and yields of the products were checked with quantitative vapor-phase chromstography. Identification of these products was performed by comparison of their infrared spectra with those of authentic samples. Other reactions of triphenylsulfonium bromide with *p*-toluenethiolate and thiophenoxide ions were carried out similarly to the above reaction. All the results are summarized in Table 4.

**The Reaction of Diphenylethoxysulfonium Tetrafluoroborate with Sodium *p*-Toluenethiolate.** Diphenyl sulfoxide (2 g, 0.01 mol) was dissolved in anhydrous methylene chloride (5 m*l*) containing triethyloxonium tetrafluoroborate (2 g). The reaction mixture was stirred for about 30 min, at room temperature and to the this solution 50 m*l* of anhydrous ether was added, then the methylene chloride-ether mixture was replaced by anhydrous ethanol (30 m*l*) by decantation. To this solution was slowly added sodium *p*-toluenethiolate (1.46 g, 0.01 mol) in anhydrous ethanol (20 m*l*) −5—−10°C over a period of about 1 hr with stirring. After stirring was continued for 30 min, the reaction mixture was poured into ice water, acidified carefully with dilute cold hydrochloric acid, extracted with a large amount of ether, washed and dried over magneisum sulfate. From the ether layer, diphenyl sulfide (42%) and di-*p*-tolyl disulfide (40%) were isolated. The yields of products were determined by quantitative vapor phase chromatography.

**Sodium *p*-Toluenethiolate.** The compound was prepared by treating *p*-tolyl mercaptan (10 g, 0.08 mol) and sodium hydroxide (3.7 g, 0.078 mol) in benzene. The usual work up of the reaction mixture afforded 11 g of colorless sodium *p*-toluene thiolate in 94 % yield.

**The Reaction of Triarylsulfonium Bromide with Potassium Hydroxide in Aqueous Ethanol and Water.** A typical run is as follows. Triphenylsulfonium bromide (1 g, 0.003 mol) and potassium hydroxide (1.3 g, 0.0024 mol) were dissolved in water. The solution was sealed into a glass tube and heated for 50 hr at 150—160°C. After cooling, the sealed tube was broken and the content poured into water, acidified with dilute hydrochloric acid, extracted with ether, washed, dried over magnesium sulfate. The ether layer was fractionated by vapor phase chromatography. Identification and determination of the yields of the products were also done by IR, NMR and gas chromatography. All the results and those from other reaction are shown in Tables 3 and 4.

**Kinetic Experiment.** Kinetic measurement and the rate calculation of alkaline decomposition of triphenylsulfonium bromide with ethoxide ion in aqueous ethanol were performed with the use of the ultraviolet spectra of the diphenyl sulfide in the same method as described previously.[2)]