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DECOMPOSITION OF TRIARYLSULFONIUM ALKOXIDES

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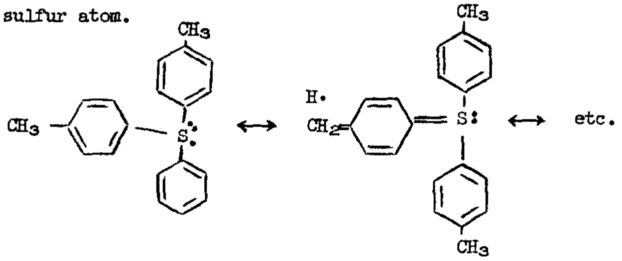
In a previous communication (1) we have suggested that the mechanism of pyrolysis of triarylsulfonium halides to give diaryl sulfides and the corresponding aryl halides involves the addition of the halide ion to the sulfur atom of the sulfonium cation and subsequent intramolecular collapse of the adduct. We have now carried out a study of the decomposition of triarylsulfonium alkoxides, and the results are summarized in Table 1.

It is clear that the complex mixture of products produced in each case precludes a rationalization based on the operation of a simple and exclusive aromatic S_N1 mechanism or bimolecular aromatic nucleophilic substitution process. In fact, the only single mechanism able to accommodate all the facts is a radical process analogous to that suggested for the decomposition of various diaryliodonium salts (2-11). The gross features of the mechanism, as applied to triarylsulfonium alkoxides, are as follows:

(a) $\mathrm{Ar_3S^+, OCHR_2^-} \rightleftharpoons \mathrm{Ar_3SOCHR_2} \rightleftharpoons (\mathrm{Ar_3\dot{S}, R_2CH\dot{O}})$
(b) $(\mathrm{Ar_3\dot{S}, R_2CH\dot{O}}) \longrightarrow \mathrm{Ar_2S + ArOCHR_2}$
(c) $(\mathrm{Ar_3\dot{S}, R_2CH\dot{O}}) \longrightarrow \mathrm{Ar_3S\cdot + R_2CHO\cdot}$
(d) $\mathrm{Ar_3S\cdot} \longrightarrow \mathrm{Ar_2S + Ar\cdot}$
(e) $\mathrm{Ar\cdot + R_2CHOH} \longrightarrow \mathrm{ArH + R_2\dot{C}OH}$
(f) $\mathrm{R_2CHO\cdot + R_2CHOH} \qquad \mathrm{R_2CHOH + R_2\dot{C}OH}$
(g) $\mathrm{2\ R_2\dot{C}OH} \longrightarrow \mathrm{RCOR + R_2CHOH}$

The outstanding features of the data presented in Table 1 are readily understood in terms of this mechanism. (1) The major products of the decomposition reactions are alkyl aryl ethers, diarylsulfides, aromatic hydrocarbons and ketones (or aldol resins derived from aldehydes). (2) In the reaction of diphenyl-p-tolylsulfonium bromide with sodium tert-butoxide, trace amounts of acetone and an alkane of low molecular weight were detected. These could only have arisen by the decomposition of the tert-butoxyl radical. Also, a host of unidentified products were formed, these probably arising by attack of various reactive radicals on the primary products. The NMR spectra of some of these products suggested the presence of tert-butoxyl and aromatic methyl groups. (3) In the reaction of triphenylsulfonium iodide with sodium isopropoxide in isopropyl alcohol solution, the ratio of isopropyl phenyl ether to benzene produced was about 2:1. In the identical reaction with triphenylsulfonium bromide, the ratio was about 49:1. Similar results were obtained with other alkoxides. Although a precise explanation for these observations cannot be offered at the present time, the sensitivity of product ratios to the halide ion present in solution is a phenomenon which has been observed for other radical processes (12). (4) It is striking that decomposition of triphenylsulfonium bromide by the action of sodium isopropoxide gives but a 2% yield of benzene (and acetone), whereas the similar reaction of tri-p-tolylsulfonium bromide with sodium isopropoxide affords a 77% yield of toluene (and acetone). The more reactive the radicals in the radical pair ($Ar_3\dot{S}$, $R_2CH\dot{O}$), the greater will be the yield of alkyl aryl ether and diaryl sulfide. The more stable the radicals that make up the radical pair, the greater is the likelihood of the radicals becoming free from one another and reacting with the solvent, this giving rise to the sequence of reactions that produces the aromatic hydrocarbons plus the carbonyl compounds. The larger yield of toluene in the reactions of tri-p-tolylsulfonium bromide with sodium alkoxides than that of benzene in the corresponding reactions of triphenylsulfonium bromide may be attributable to the greater stability of the tri-p-tolylsulfur radical over the triphenylsulfur radical.* The enhanced stability of the tri-p-tolylsulfur radical can be attributed to a type of hyperconjugation involving use of the d-orbitals of the sulfur atom.



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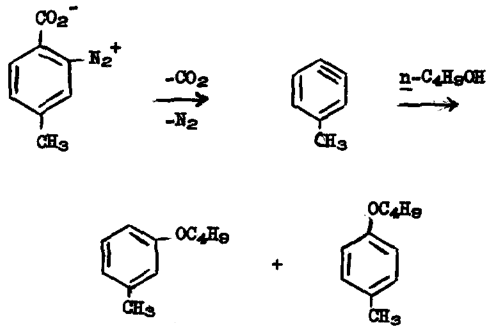
*There is electrochemical evidence for the existence of the triphenylsulfur radical (13-15).

An argument could be made that the diaryl sulfides plus the corresponding aryl alkyl ethers arise by a bimolecular aromatic nucleophilic substitution process, while the aromatic hydrocarbons plus ketones (or aldehydes) result from a competing reaction analogous to the Meerwein-Ponndorf-Verley reaction. The combination of these reactions cannot be used to explain the formation of acetone and the large number of by-products in the diphenyl-*p*-tolylsulfonium tert-butoxide decomposition reaction, and explanations of product ratios produced in the various reactions would be unsatisfactory. However, it is possible, particularly in view of the results of the reaction of triphenylsulfonium iodide with sodium *n*-butyl mercaptide, that the bimolecular aromatic nucleophilic substitution process occurs concomitantly with the radical process.

Another possibility worthy of consideration is that the diaryl sulfides and alkyl aryl ethers arise by a mechanism in which a benzyne type of intermediate is generated by attack of the alkoxide ion on the triarylsulfonium cation. Benzynes have been postulated as being intermediates in other reactions between triarylsulfonium cations and bases (16,17). This possibility was ruled out for the triarylsulfonium alkoxide decomposition reactions on the basis of the following experimental observations: (a) The reaction of tri-*p*-tolylsulfonium bromide with sodium *n*-butoxide gave *n*-butyl *p*-tolyl ether as the sole alkyl aryl ether. (b) Decomposition of the dipolar ion derived by diazotization of 2-amino-4-methylbenzoic acid, a type of reaction known (18) to give a benzyne type of intermediate, in *n*-butyl alcohol afforded *n*-butyl *m*-tolyl ether and *n*-butyl *p*-tolyl ether in a 65:35 ratio.



The various sulfonium halides used in these studies were prepared by adaptations of the methods of Makarova and Nesmeyanov (5), Wildi, Taylor and Potratz (19) and Courtot and Tung (20). The structures and purities of the salts were established by carrying out pyrolyses, which afford diaryl sulfides and the corresponding aryl halides in quantitative yield (1), with subsequent vapor phase chromatographic analyses of the product mixtures.

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Table 1

Reactions of Triarylsulfonium Halides with Alkoxide Ions

Triarylsulfonium Halide	RO^-, in Solvent ROH	Temp. °C.	Time, hr.	Products, %			
				Hydrocarbon	Ether	Sulfide	Carbonyl Compound
$(C_6H_5)_3\overset{+}{S}$, I^-	CH_3O^-	64	116	16	56	88	resins
"	$C_2H_5O^-$	78	24	19	46	95	aldol resins
"	$n\text{-}C_4H_9O^-$	116	24	9	86	98	aldol resins
"	$(CH_3)_2CHO^-$	80	39	25	52	100	acetone, 29
$(C_6H_5)_3\overset{+}{S}$, Br^-	$C_2H_5O^-$	78	24	<7	69	95	aldol resins
	$n\text{-}C_4H_9O^-$	116	24	1	98	98	aldol resins
	$(CH_3)_2CHO^-$	80	39	2	97	98	acetone, trace
$(p\text{-}CH_3C_6H_4)_3\overset{+}{S}$, Br^-	CH_3O^-	64	116	38	24	68	resins
	$C_2H_5O^-$	78	24	48	9	85	aldol resins
	$n\text{-}C_4H_9O^-$	116	24	21	73	96	aldol resins
	$(CH_3)_2CHO^-$	80	39	77	15	99	acetone, 70
$(C_6H_5)_3\overset{+}{S}$, I^-	$n\text{-}C_4H_9S^-$ in $n\text{-}C_4H_9OH$	116	24	1	77 $(C_4H_9SC_6H_5)$	97	
$p\text{-}CH_3C_6H_4\overset{+}{S}(C_6H_5)_2$ Br^-	$CH_3CH_2O^-$	78	24	3$(C_6H_5CH_3)$	13.8 $(p\text{-}CH_3C_6H_4OC_2H_5)$	72 $(p\text{-}CH_3C_6H_4SC_6H_5)$ + 11.2 $(C_6H_5)_2S$	aldol resins
$p\text{-}CH_3C_6H_4\overset{+}{S}(C_6H_5)_2$ Br^-	$(CH_3)_3CO^-$	83	24	Traces[a]	17.8 $(C_6H_5OC(CH_3)_3)$ + 5.7 $(p\text{-}CH_3C_6H_4OC(CH_3)_3)$	58.9 $(p\text{-}CH_3C_6H_4SC_6H_5)$ + 12.4 $(C_6H_5)_2S$	acetone, trace

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[a] Benzene, toluene and an alkane of low mol. wt. were present. Small amounts of several unidentified compounds were detected by GLPC analysis. Also, much

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