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COMPETING MODES OF DECOMPOSITION OF TRIARYLSULFONIUM ALKOXIDES

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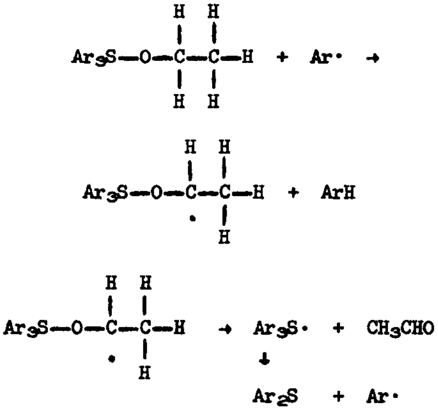
The reaction of a triarylsulfonium halide with a sodium alkoxide in a solution in the corresponding alcohol at an elevated temperature produces a mixture of aromatic hydrocarbon, alkyl aryl ether, diaryl sulfide and aldol resin (or a ketone if the alkoxide is derived from a secondary alcohol).[1,2] Frequently, a small amount of biaryl is also produced. We have suggested previously that the aromatic hydrocarbon, biaryl, and ketone or aldehyde (which subsequently forms a resin in the strongly basic medium) are formed by a free radical process, whereas the alkyl aryl ether is produced by a competing aromatic nucleophilic displacement reaction, and we have provided some evidence in support of this interpretation.[1,2] Oae and Khim,[3] on the other hand, have suggested that both the aromatic hydrocarbon plus aldehyde (or ketone) and the alkyl aryl ether arise by competing ionic sequences of reactions. We have now uncovered evidence which clearly indicates that the aromatic hydrocarbon and carbonyl compound are the products of a free radical chain reaction, whereas the alkyl aryl ether is the product of an aromatic nucleophilic displacement reaction.

The evidence for the competing radical and ionic pathways, as applied to the reaction of diphenyl-p-tolylsulfonium iodide (I) with sodium ethoxide in ethanol solution, is as follows: (1) The reaction of 0.001 mole of I with 0.003 mole of sodium ethoxide in 3.00 ml. of absolute ethanol in a sealed tube at 80° for 24 hours affords benzene (41.4% yield), toluene (14.1%), phenetole (22.1%), diphenyl sulfide (19.3%) and phenyl p-tolyl sulfide (84.0%) as the major products when no effort is made to remove oxygen of the air from the system. These and additional data are shown in Table 1. When the same reaction is carried out on a degassed solution in an argon atmosphere, the major products and yields are benzene (62.8%), toluene (20.6%), phenetole (11.5%), diphenyl sulfide (19.3%) and phenyl p-tolyl sulfide (75.0%). Clearly, oxygen or a peroxide is functioning as an inhibitor of a chain reaction which produces benzene and toluene; however, the presence of oxygen does not affect the rate of production of phenetole, which arises by a conventional aromatic nucleophilic displacement reaction. Thus, the presence of even a very small amount of oxygen causes the yields of aromatic hydrocarbons to decrease, and, by default, more of the product of the competing displacement reaction to be formed. (2) The effect is even more dramatic when certain additives are present. For example, when 0.001 mole of 1,1-diphenylethylene is added to the reaction mixture, the major products and yields are benzene (8.0%), toluene (2.3%), phenetole (75.5%), p-methylphenetole (2.1%), diphenyl sulfide (8.2%) and phenyl p-tolyl sulfide (92.5%); 1,1-diphenylethylene is recovered unchanged in 87.5% yield. Thus, in relatively high concentration, 1,1-diphenylethylene is effectively inhibiting the radical chain reaction leading to the formation of aromatic hydrocarbons, presumably by capturing aryl radicals.[4]

The effects of such well known radical traps as galvinoxyl and diphenylpicrylhydrazyl on the system under consideration are of interest, but subject to some ambiguity in interpretation owing to the fact that these radicals can undergo reactions with strong bases. When 5×10^{-5} mole of diphenylpicrylhydrazyl is added to the reaction mixture described above, without exclusion of oxygen, the major products are benzene (54.1%), toluene (16.5%), phenetole (18.9%), diphenyl sulfide (18.8%) and phenyl p-tolyl sulfide (77.0%). With the same amount of diphenylpicrylhydrazyl present, but with exclusion of oxygen (argon atmosphere), the products are benzene (39.7%), toluene (14.1%), phenetole (28.7%), diphenyl sulfide (17.7%) and phenyl p-tolyl sulfide (78.0%). Evidently, when both oxygen and diphenylpicrylhydrazyl, each of which functions as an inhibitor of the radical chain reaction in its own right, are present in small concentrations, they neutralize each other. Indeed, diphenylpicrylhydrazyl is known to form a complex with oxygen.[5]

The presence of 5×10^{-5} mole of galvinoxyl in the reaction mixture, with or without exclusion of oxygen, leads to the production of benzene (48-50%), toluene (16.8%), phenetole (23.0-24.6%), diphenyl sulfide (18.7%) and phenyl p-tolyl sulfide (81.5-83.5%). Thus, the amount of galvinoxyl surviving reaction with base[6] appears to inhibit somewhat the production of aromatic hydrocarbons, but not that of phenetole. Even when a relatively large amount of galvinoxyl (0.001 mole) is added to the reaction mixture, the yield of phenetole is not decreased noticeably. Since galvinoxyl is known to be an efficient trap for alkoxyl radicals,[7] it is apparent that phenetole is not arising by a radical reaction involving ethoxyl radicals. Furthermore, the fact that phenetole is produced, almost to the exclusion of p-methylphenetole, constitutes valid additional evidence for the aromatic nucleophilic displacement process.[1,2,8]

We suggest that the mechanism of formation of initiator radicals is the same as that described previously.[1,2] We further suggest that the chain propagation steps in the radical reaction leading to the production of aromatic hydrocarbons are as follows:



$$Ar_3S{-}O{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H + Ar\cdot \rightarrow$$

$$Ar_3S{-}O{-}\underset{\cdot}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H + ArH$$

$$Ar_3S{-}O{-}\underset{\cdot}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H \rightarrow \begin{array}{l} Ar_3S\cdot \quad + \quad CH_3CHO \\ \downarrow \\ Ar_2S \quad + \quad Ar\cdot \end{array}$$

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6. In a control experiment we found that not more than 17% of a 0.001 mole quantity of galvinoxyl remains unchanged after a 24 hour period of reaction with 0.003 mole of sodium ethoxide in 3 ml. of ethanol at 80°.
7. P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).
8. 2-Nitrobromobenzene undergoes an aromatic nucleophilic displacement reaction with piperidine about seven times faster than does 2-nitro-4-methylbromobenzene: E. Berliner

and L. C. Monack, *J. Amer. Chem. Soc.*, **74**, 1574 (1952). An electronic effect of about this size together with statistical considerations (two phenyl groups *vs.* one *p*-tolyl group) accounts for the fact that only a very small amount of *p*-methylphenetole is formed in an aromatic nucleophilic displacement reaction of ethoxide ion on the diphenyl-*p*-tolylsulfonium cation. In the competitive formation of aryl radicals by the thermal decomposition of hydroxytriphenyl-*p*-tolylantimony, however, there is a slight discrimination in favor of the *p*-tolyl radical: F. L. Chupka, Jr., Ph.D. Dissertation, University of Massachusetts, Amherst, Massachusetts, 1968.

Table 1

Reaction of Diphenyl-*p*-tolylsulfonium Iodide (0.001 mole) with Sodium Ethoxide (0.003 mole) in Ethanol (3 ml.) at 80° for 24 hr. in Sealed Tube

Atmosphere	Additive	% Yield Products						
		C_6H_6	C_6H_5Me	C_6H_5OEt	*p*-Me-C_6H_4OEt	Ph_2S	PhSTol	Biphenyl
Air	None	41.4	14.1	22.1	0.8	19.3	84.0	1.5
Argon	None	62.8	20.6	11.5	trace	19.3	75.0[a]	
Air	1,1-Diphenylethylene[b]	8.0	2.3	75.5	2.1	8.2	92.5	
Air	Diphenylpicrylhydrazyl[c]	54.1	16.5	18.9	trace	18.8	77.0	trace
Argon	Diphenylpicrylhydrazyl[c]	39.7	14.1	28.7	1.0	17.7	78.0	
Air	Galvinoxyl[c]	48.1	16.8	24.6	0.9	18.8	83.5	trace
Argon	Galvinoxyl[c]	50.0	16.8	23.0	trace	18.7	81.5	trace
Air	Galvinoxyl[d]	22.5	6.9	18.2		23.2	77.5	1.0

[a] Note close correspondence between yields of diphenyl sulfide and toluene and between phenyl *p*-tolyl sulfide and benzene plus phenetole.

[b] 0.001 mole, of which 87.5% is recovered unchanged

[c] 0.00005 mole

[d] 0.001 mole