A New Mechanism for Photodecomposition and Acid Formation from Triphenylsulphonium Salts

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A new photodecomposition pathway for triphenylsulphonium salts yields phenylthiobiphenyls by a cage fragmentation–recombination process as major products, in addition to diphenyl sulphide; a new mechanism for acid formation is described.

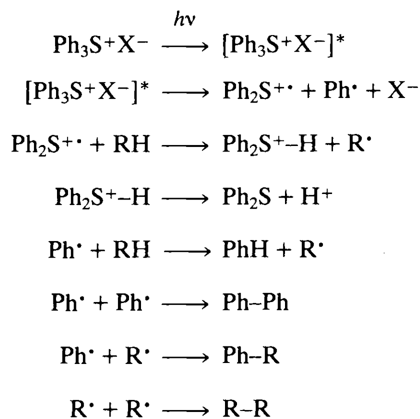
Triphenylsulphonium salts have recently become important as photoinitiators for acid catalysed processes in resist applications.[1] The proposed mechanisms for photodecomposition and subsequent acid formation involve homolysis (Scheme 1) or heterolysis (Scheme 2) reactions from the excited state of the sulphonium salt. Homolytic cleavage generates the diphenylsulphinyl radical cation which abstracts a hydrogen atom from the solvent and ultimately decomposes to produce a Brönsted acid and diphenyl sulphide.[2] Heterolysis from the excited state gives diphenyl sulphide and phenyl cation as the source of acid.[3] An attempt to quantify acid production with diphenyl sulphide formation resulted in an excess of acid in a 3:1 ratio.[4] One explanation for excess acid formation was attack on diphenyl sulphide by the diphenylsulphinyl radical cation resulting in production of acid and the diphenyl(4-phenylthiophenyl)sulphonium salt which could also photodecompose to give acid.[5] This mechanism requires diphenyl sulphide to be present and at best would generate a 2:1 ratio of acid to diphenyl sulphide. We report here a new photoinduced rearrangement of triphenylsulphonium salts which will generate acid and rationalise the excess acid phenomenon.

Irradiation of a 0.01 M acetonitrile solution of triphenylsulphonium bromide, trifluoromethanesulphonate, hexafluoroantimonate, hexafluorophosphate, or tetrafluoroborate to low conversion (<10%) in a Rayonet reactor (λ = 254 nm) yields previously unobserved 2-phenylthiobiphenyl (**2**) as the major product, along with 3-phenylthiobiphenyl (**3**), 4-phenylthiobiphenyl (**4**), and the known photoproduct diphenyl sulphide (**1**) (Scheme 3).† Furthermore, irradiation of triphenylsulphonium trifluoromethanesulphonate in methanol and ethanol gives (**2**) as the major product along with its isomers and diphenyl sulphide. The product ratios are shown in Table 1. The selectivity of rearrangement products, (**2**) > (**4**) > (**3**) remains reasonably constant, whereas the ratio of total phenylthiobiphenyl isomers to diphenyl sulphide is solvent dependent. Acid generation from the photolyses was

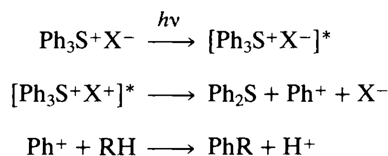
† All photoproducts were identified by g.c. retention times and compared with authentic samples obtained commercially. The phenylthiobiphenyl isomers were synthesised from the respective bromobiphenyls by the method of J. R. Campbell, *J. Org. Chem.*, 1964, **20**, 1830. The *ortho* and *para* isomers were previously reported by P. M. Brown, P. S. Dewar, A. R. Forrester, and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2842, and R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, 1957, **29**, 277.

Table 1. Photoproduct distribution from irradiation of triphenylsulphonium trifluoromethanesulphonate.†

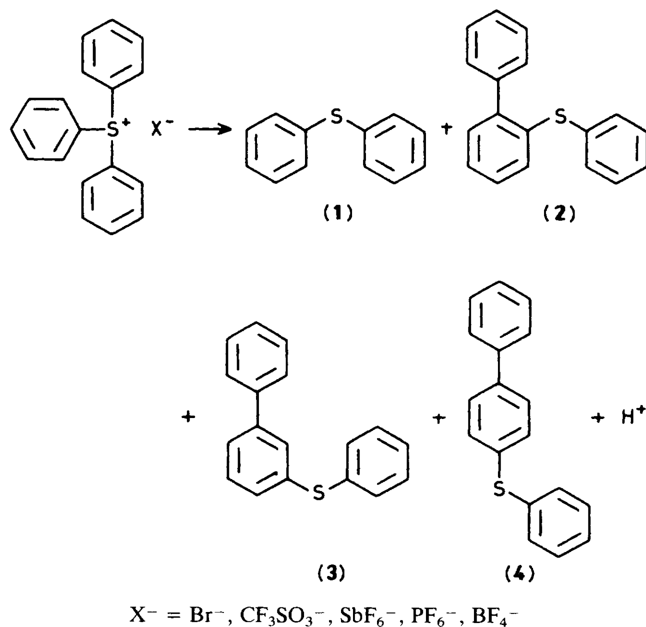
Solvent	(1)	(2)	(3)	(4)	Total	[(2) + (3) + (4)]/(1)	Acid/$\times10^{-4}$ M
	/$\times10^{-4}$ M						
MeCN	3.8	4.5	0.5	0.9	9.7	1.53	11.5
MeOH	3.2	4.3	0.4	0.8	8.7	1.72	13.7
EtOH	2.0	4.0	0.4	0.6	7.0	2.50	10.5



Scheme 1. Homolytic photodecomposition pathway for triphenylsulphonium salts.



Scheme 2. Heterolytic photodecomposition pathway for triphenylsulphonium salts.



Scheme 3. Products from irradiation of triphenylsulphonium salts.

measured by a non-aqueous photometric method using sodium 4-nitrophenoxide solutions in acetonitrile standardized with trifluoromethanesulphonic acid. Acid produced photochemically does not correlate with diphenyl sulphide formation in each solvent yet correlates reasonably well with total product formed, including all three phenylthiobiphenyl isomers and diphenyl sulphide.

Photolysis of the triphenylsulphonium salt produces an excited state which can undergo homolysis to the phenyl radical and diphenylsulphinyl radical cation or heterolysis to phenyl cation and diphenyl sulphide. If the phenyl radical or phenyl cation escapes from the solvent cage, decomposition can occur by the mechanism shown in Schemes 1 and 2 to produce diphenyl sulphide and acid. If escape does not occur, recombination will result. Direct recombination inside the solvent cage can yield the triphenylsulphonium salt, whereas recombination by molecular rearrangement yields the three phenylthiobiphenyl isomers. The selectivity *ortho* > *para* > *meta* observed in the solvent cage products is consistent with either homolytic or heterolytic cleavage. The escape products include biphenyl, presumably formed by phenyl radical dimerization, and phenylacetamide in acetonitrile or anisole in methanol suggesting a phenyl cation intermediate. The rearrangement products also yield acid. This is confirmed by the change in ratio of cage to non-cage products upon varying the solvent. If diphenyl sulphide formation is the only pathway to generate acid, then the acid produced should decrease as the proportion of cage products increases. Table 1 shows that the proportion of cage reaction (phenylthiobiphenyls/diphenyl sulphide) increases significantly with solvent viscosity while acid generated does not decrease.

The photoinitiated homolytic cleavage and molecular rearrangement described above is similar to the Photo-Fries reaction.[6] A low yielding photorearrangement has also been observed in a thianthrenium salt system.[7] It should be noted that in resist formulations where triphenylsulphonium salts are used, the viscosity effect is larger than in solution and the photoinduced rearrangement may be the only pathway to generate acid.

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