Thiosulphonium Ion Intermediate in the Oxidation of a Thiol with Dimethyl Sulphoxide

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Summary A thiosulphonium ion was isolated as intermediate in the oxidation of a thiol to a disulphide with dimethyl sulphoxide; the reactions of the ion are described.

THIOLS are oxidized to disulphides with sulphoxides,[1] and the oxidation has been suggested to proceed *via* an unstable thiol–sulphoxide adduct such as a thiosulphonium ion.[2] The isolation of the thiosulphonium ion is of interest in connection with the possibility of an attack of a sulphide sulphur atom on a sulphonium sulphur cation.[3]

Here we report the isolation of a thiosulphonium ion during the oxidation of 4-methylbenzenethiol (**1**) with Me_2SO in the presence of $(CF_3CO)_2O$. In a typical procedure, solutions of $(CF_3CO)_2O$ (3 equiv.) and (**1**) in dry CH_2Cl_2 were successively added to a solution of Me_2SO (3 equiv.) in dry CH_2Cl_2 at −80 °C. After evaporation of the solvent and Pummerer rearrangement[4] products *in vacuo* at room temperature, the residue was washed with dry hexane. The thiosulphonium ion (**2**) was obtained as a yellow liquid in 90% yield (Scheme) [δ($CDCl_3$) 2·48 (3H, s, Me–C), 2·89 (6H, s, Me–S^+), 7·40 (2H, d), and 7·60 (2H, d)].

$$Me_2SO + (CF_3CO)_2O \rightarrow [Me_2S^+(OCOCF_3)]CF_3CO_2^-$$

$$4\text{-}MeC_6H_4SH\ (\mathbf{1}) \downarrow \quad -CF_3CO_2H$$

$$[Me_2S^+(SC_6H_4Me\text{-}4)]CF_3CO_2^-\ (\mathbf{2})$$

SCHEME

On keeping at room temperature for several hours, (**2**) partially decomposed into $(4\text{-}MeC_6H_4)_2S_2$ (**3**) and some unidentified compounds. The ion (**2**) is sensitive to water and on contact is decomposed quantitatively into (**3**) and $4\text{-}MeC_6H_4SSO_2C_6H_4Me\text{-}4$.

Compound (**2**) was also prepared from $4\text{-}MeC_6H_4SCl$, dimethyl sulphide, and silver trifluoroacetate in a manner similar to that described for the preparation of thiosulphonium perchlorate.[5]

Treatment of (**2**) with (**1**) instantly generated (**3**) in 98% yield. This means that (**2**) is an intermediate in the oxidation of (**1**) to (**3**). Treatment of (**2**) with 2-methylpropane-2-thiol afforded t-butyl tolyl disulphide in 87% yield, but no symmetrical disulphides were detected.

The ion (**2**) rapidly reacted with cyclohexene at room temperature to give 1-(4-tolylthio)-2-trifluoroacetoxy-cyclohexane [50% yield; b.p. 130 °C at 0·8 mmHg; δ(CCl_4) 1·2—2·2 (8H, m, CH_2), 2·34 (3H, s, Me), 3·02 (1H, m, CH–S), 4·88 (1H, m, CH–O), 7·08 (2H, d), and 7·30 (2H, d); ν_{max} 1780 cm^{-1} (C=O); *m/e* 318 (M^+)]. Treatment of (**2**), like thiosulphonium perchlorate,[5] with anisole afforded 4-methoxyphenyl tolyl sulphide [48% yield; b.p. 145 °C at 0·8 mmHg; δ(CCl_4) 2·29 (3H, s, Me), 3·75 (3H, s, Me–O), 6·80 (2H, d), 7·04 (4H, s), and 7·32 (2H, d)]. This suggests that the isolated intermediate (**2**) resembles thiosulphonium perchlorate.

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[1] A. Ohno and S. Oae in 'Organic Chemistry of Sulfur,' ed. S. Oae, Plenum Press, New York, 1977, p. 159.
[2] T. J. Wallace and J. J. Mahon, *J. Amer. Chem. Soc.*, 1964, **86**, 4099.
[3] T. Numata and S. Oae, *Internat. J. Sulfur Chem., A*, 1971, **1**, 6; R. Tanikaga, K. Nakayama, K. Tanaka, and A. Kaji, *Chem. Letters*, 1977, 395; A. Bovio and U. Miotti, *J.C.S. Perkin II*, 1978, 172.
[4] K. Omura, A. K. Sharma, and D. Swern, *J. Org. Chem.*, 1976, **41**, 957.
[5] H. Minato, T. Miura, and K. Kobayashi, *Chem. Letters*, 1975, 1055.