

# DEUTERIUM STUDIES IN THE DISPROPORTIONATION OF THIOXANTHYLIUM SALTS

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## Abstract

Deuterium labelling is used to show that the disproportionation of thioxanthylum salts involve transfer of a hydride, (deuteride) ion from the 9 - position of one molecule of the compound, as its hydrol, to the 9 - position of another molecule in the cation form.

## Introduction

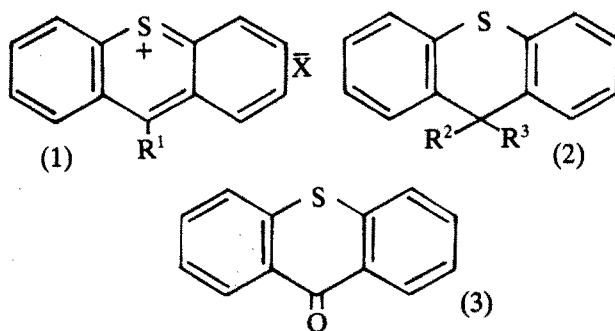
Thioxanthylum salts (1) without a 9 - substituent may undergo acid - induced disproportionation to the corresponding thioxanthene (2;  $R^2 = R^3 = H$ ) and thioxanthone (3) [1, 2]. Disproportionation of similar compounds i. e. acridinium salts [3] (4;  $R' = Me, R^2 = H, D, X^- = I$ ) have been proved to involve transfer of a hydride ion from the 9 - position of the pseudo - base form of the compound to the 9 - position of the salt, and it seemed likely that the reaction undergone by thioxanthylum salts is analogous. Here, we report our investigation for the case of thioxanthylum chloride (1;  $R^1 = H, X = Cl$ ).

## Results and Discussion

Treatment of thioxanthylum perbromide [4] (1;  $R = H, X = Br_3^-$ ) with alkali as have been described for acridinium salts, [3] resulted thioxanthone (3) as the only identified product. It seemed highly probable that in alkali the thioxanhydrol (2;  $R^3 = OH$ ) form is much more stable than the corresponding species in the acridine series and little or none of the salt form is present at equilibrium. This interpretation was supported by the fact that a mixture of thioxanthylum perbromide (1) and preformed thioxanhydrol [5-6] (2;  $R^3 = OH$ ) in a non - hydroxylic solvent such as tetrahydrofuran, gave a steam volatile mixture of thioxanthene (2;  $R^2 = R^3 = H$ ) and thioxanthone (3). Both compounds were identical to the samples made

unambiguously [7, 8]. The same salt underwent disproportionation with 4N - hydrochloric acid to thioxanthene (2) and thioxanthone (3). The quantitative yield of both thioxanthene and thioxanthone in the reaction mixture was determined by  $^1H$ . n. m. r. spectroscopy and by using 3, 5 - dimethyl pyrazole as internal standard. The equimolar ratio of the above compounds indicate that thioxanthene, unlike the corresponding species in the acridine series, do not undergo partial oxidation to thioxanthone.

[9- $^2H$ ] thioxanhydrol (2;  $R^2 = ^2H, R^3 = OH$ ) was prepared by reducing thioxanthone (3) by sodium [ $^2H$ ] borohydride in boiling tertiary butanol. The product was shown by  $^1H$ . n. m. r. and mass spectrometry to have an isotopic purity  $>95\%$ . This compound underwent disproportionation on treatment with acid as described for unlabelled compound.



The product which was separated by steam distillation proved to be the steam volatile [9'9- $^2H_2$ ] thioxanthene (2;  $R^2 = R^3 = ^2H; 25\%$ ) with a high degree of isotopic

Key words: Disproportionation Thioxanthylum Salts

purity >95% and the non volatile thioxanthone (3; 26.5%). The reaction was repeated using an unlabelled specimen of thioxanthrydrol (2;  $R^2 = H, R^3 = OH$ ) and a mixture of deuterium oxide and deuterium chloride. The product was shown to be thioxanthene (2;  $R^2 = R^3 = H$ ) with no detectable deuterium and thioxanthone (3). The results of these experiments clearly indicate that the extra hydrogen atom aquired by a thioxanthylum salt comes exclusively from the 9- position of a thioxanthrydrol molecule. It seems likely that the reaction proceeds through an ionic mechanism, since, the transfer of the hydride ion occurs to a cationic species, and that it proceeds in a good ionizing medium. The possible mechanism of this reaction is depicted in the scheme.

This reaction is reminiscent of other related disproportionation of xanthylum [8], pyrimido [4, 5-b] quinolinium [9] and other similar salts [10], but labelling evidence has only been produced for pyrimido [4, 5-b] quinolinium salts.

### Experimental Section

Mass spectra were measured on an AEI MS 902s Spectrometer with source temperature, ca. 220°C, accelerating voltage 8 kv, trap current 500 MA and

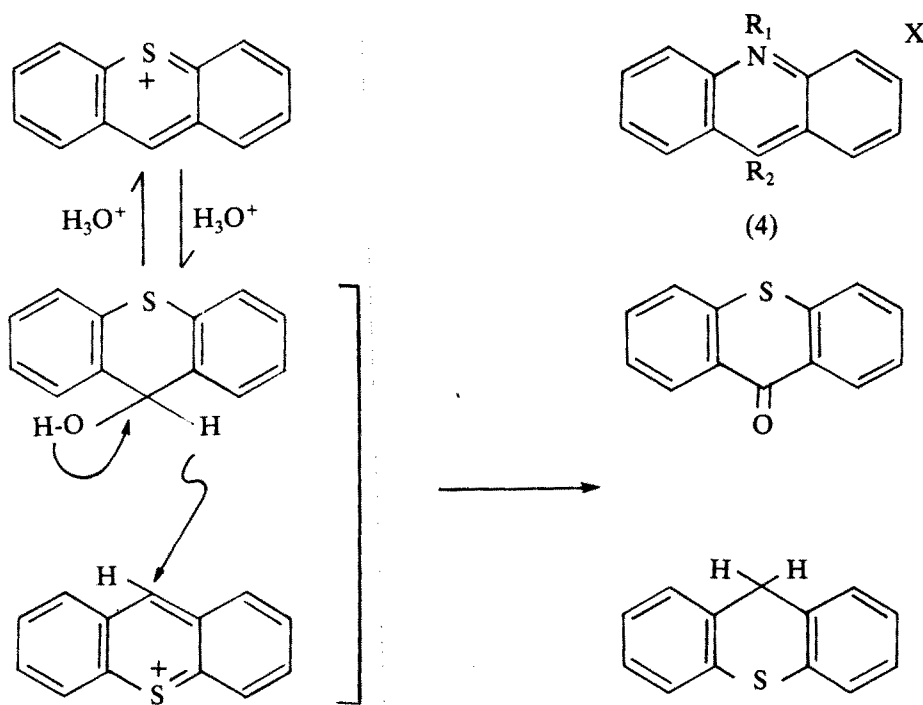
ionising energy 70 ev, except where otherwise stated.  $^1H$  N.M.R. spectra for  $CDCl_3$  were measured on a Perkin - Elmer R32 spectrometer at normal probe temperature, using tetramethyl - silane as internal standard.

#### [9- $^2H$ ] thioxanthrydrol

A mixture of thioxanthone (0.5 g) and sodium [ $^2H$ ] borohydride (0.5 g) in tertiary butanol (30 ml) was refluxed for two hours. The solvent was evaporated under reduced pressure and the residue was recrystallised from pet - ether (80 - 100°) to give the title compound (0.3 g), m.p. 103°,  $\tau$  3.4 - 3.9 (8 H, m, aromatic), (Found  $M^+$  215.0494,  $C_{13}H^2HOS$ , requires  $M^+$  215.0498).

#### Disproportionation of [9- $^2H$ ] thioxanthrydrol

[9- $^2H$ ] Thioxanthrydrol (0.5 g) in 4N - hydrochloric acid (5 ml) was stirred under nitrogen for 24 hours. The solid was filtered off and steam distilled. The nonvolatile solid which remained was filtered off and crystallised from glacial acetic acid to give thioxanthone (0.13 g), m.p. 207° (lit 209°),  $\tau$  1.4 (2H, d, J 10 Hz, 1- and 8-H) and  $\tau$  2.3-2.5 (6H, m, 2-, 3-, 4-, and 7-H). The steam - volatile compound was filtered off and crystallised from ethanol-chloroform (5:1) (0.12 g), m.p. 128 - 129°,  $\tau$  2.5-2.9 (8H, m, aromatic), Found



(SCHEME)

M<sup>+</sup>, 200.0622, C<sub>13</sub>H<sub>8</sub><sup>2</sup>H<sub>2</sub>S. requires M<sup>+</sup>, 200.0627).

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