Off-line reaction monitoring with Raman spectroscopy of low concentration oxidation of alkenes in water using the dried drop concentration method

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Supporting information

Comments on the synthesis and characterisation of 4-oxirane-phenyl-sulfonate

- ¹⁰ The detergent properties of sodium alkylbenzene sulfonates frequently do not allow the use of conventional solvents and methods of organic chemistry for isolation and purification. The preparation of 4-oxirane-phenyl-sulfonate from styrene-*p*-sulfonate was achieved readily by epoxidation however, the generation of the unwanted diol product rendered separation and purification of the epoxide a challenge. The synthesis of the epoxide of styrene sulfonate was attempted in three ways.
- Initially, the epoxidation of styrene sulfonate was carried out using a modified method described by Hage *et al.*¹ Styrene sulfonate (2.06 g, 10 mmol) and $[Mn_2O_3(tmtacn)_2](PF_6)_2.H_2O$ (80 mg, 0.1 mmol, 1 mol%) was dissolved in double distilled water (100 ml). The reaction mixture was stirred and cooled in ice for 30 min. Hydrogen peroxide (50 %, 2.83 mL, 50 mmol, 5 equiv.) was added dropwise over 1 h. The reaction mixture was stirred for a further 2 h and then the water removed by lyophilisation.
- ²⁰ h. The reaction mixture was stirred for a further 2 h and then the water removed by lyophilisation. ¹H NMR and Raman spectroscopic analysis indicated the formation of both epoxide and diol products, however. This reaction was repeated but with only 0.1 mol% (8 mg) of **1**, and the ice bath was allowed to warm to room temperature over 19 h followed by lyophilisation. This did not lead to an improvement in selectivity.



Scheme 1 Modified method of Hage *et al.*¹

A second method, that reported by Lam *et al.*² was attempted. This method involves the direct oxidation of styrene sulfonate with *m*CPBA and is reported to form the epoxide after which the diol is formed in a subsequent reaction step by reaction in aquoues NaHCO₃. In the present study a mixture of ³⁰ styrene sulfonate (340 mg, 1.65 mmol) and *m*CPBA (415 mg, 2.40 mmol) were dissolved in water/ethanol (40 cm³, 1:1, v/v). The reaction was stirred for 2 h at 65 °C and tested periodically with bromine water until the test was negative. The solution was allowed to cool and the solvent was evaporated in vacuo. Residual *m*-chlorobenzoic acid was dissolved in acetone (300 mL) and filtered off leaving a white solid. ¹H NMR and Raman spectroscopic analysis confirmed that the diol product ³⁵ was obtained exclusively, indicating that hydrolysis with base was not in fact necessary. Inspection of the ¹H NMR data provided by the Lam *et al.*² revealed that the product reported as the epoxide was in fact the diol product, 4-(1,2-dihydroxyethyl)phenylsulfonate.

Ultimately the epoxide was obtained, despite the insolubility of styrene sulfonate in organic solvents, using the catalyst 1 in H₂O/CH₃CN under mildly acidic conditions (see main text for details).

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¹H NMR Spectroscopy

The ¹H NMR spectra of the sodium salts of 4-vinylbenzenesulfonate sodium salt (I), 4-oxirane-phenylsulfonate (II) and 4-(1,2-dihydroxyethyl)phenylsulfonate (III) are shown is *Figure S1a*, *b* and *c*, respectively. The differences are apparent as the double bond is converted to the epoxide and then the diol. The aromatic protons give rise to two doublets around 7.6 ppm as expected. The vinyl protons are give rise to three signals between 5 and 7 ppm. For the epoxide these protons are shifted upfield to 3-4.5 ppm. Ring opening of the epoxide to the diol results in a smaller shift in these proton signals.



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Fig. S1 ¹H NMR spectra of sodium salts of 4-vinylbenzenesulfonate sodium salt (I), 4-oxirane-phenyl-sulfonate (II) and 4-(1,2dihydroxyethyl)phenylsulfonate (III) in D₂O.

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Effect of surface treatment on deposit pattern and Raman spectra obtained



Fig. S2 Image of deposit from dried droplet containing 0.5 mM VBA in 0.1 M NaHCO3(aq) and Raman spectra recorded from each spot.

Comparison of VBA, OBA and 4-formylbenzoic acid in the solid state and after deposition using the DCDR method



Fig. S3 Solid state Raman spectra of VBA, OBA and 4-formylbenzoic acid



Fig. S4 Raman spectra of VBA, OBA and 4-formylbenzoic acid obtained using DCDR method using 20 mM solutions in 0.1 M NaHCO₃(aq).

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Effect on droplet size and concentration of analyte on spectra obtained by DCDR method

(b)

(c)

(d)





Fig. S5 Raman spectra of VBA obtained using DCDR method from 10 to 0.1 mM solutions (in 0.1 M NaHCO₃) using the DCDR method.



Uniformity of co-deposition of mixtures of VBA and SS as 0.2, 0.6 and 0.8 mole fraction mixtures

Figure S6 Raman spectra (after normalisation for area under the peak at 1600 cm⁻¹ and baseline correction) obtained at eight different points on deposition s ring (mole fraction was 0.2 VBA/0.8 SS)



Figure S7 Average spectrum (blue) and standard deviation (red) from average spectrum obtained at eight different points on deposition ring (mole fraction was 0.2 VBA/0.8 SS).



Figure S8 Raman spectra (after normalisation for area under the peak at 1600 cm⁻¹ and baseline correction) obtained at eight different points on deposition ring (mole fraction was 0.6VBA/0.4SS)



Figure S9 Average spectrum (blue) and standard deviation (red) from average spectrum obtained at eight different points on deposition ring (mole fraction was 0.6 VBA/0.4 SS)







5 Figure S11 Average spectrum (blue) and standard deviation (red) from average spectrum obtained at eight different points on deposition ring (mole fraction was 0.8 VBA/0.2 SS)

References

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