

The Oxidation of Alkyl Isothiocyanates by Peroxomonosulphuric Acid

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Abstract

Oxidation of methyl and ethyl isothiocyanates by peroxomonosulphuric acid in aqueous solution at 25°C has rate constants equal to 1.05 and 0.75 dm³ mol⁻¹ s⁻¹ respectively. The oxidation product was not identified.

Introduction

We have previously reported on the mechanisms of the oxidations of thiocyanate ion¹ and some short-chain alkyl thiocyanates² by peroxomonosulphate, but were unable to investigate the oxidation of methyl isothiocyanate owing to a competing side-reaction.³ We have now suppressed this side-reaction by edta addition and have studied the oxidation of methyl and ethyl isothiocyanates with the above oxidant. Both compounds consume the same number of moles of peroxomonosulphate per mole, and the reactions follow the same simple second-order rate law. The organic product has, however, not yet been identified.

Experimental

Reagents

Methyl isothiocyanate (B.D.H. laboratory reagent grade) was distilled twice before use.

Ethyl isothiocyanate was originally prepared from the reaction between Cl₂CS and EtNH₃Cl in NaOH solution at about 5°C,⁴ but the reaction between cold EtNH₂, CS₂, Et₃NH and 30% H₂O₂⁵ was found to be more convenient and give a better yield (c. 40%). In both cases, the final product was distilled twice before use (b.p. 132°C).

Peroxomonosulphate was prepared as previously reported,¹ but no effort was made to remove sulphate. Thus, the stock solution contained hydrogen peroxide at less than 10⁻³ M, peroxomonosulphate at 8.5 × 10⁻² M and sulphuric acid at 1.2 × 10⁻¹ M.

The edta (disodium salt) was B.D.H. laboratory reagent grade and recrystallized as recommended.⁶

Other chemicals were either analytical reagent grade or the best available, and were used as supplied. All water used in solution preparation and kinetic measurements was redistilled from alkaline permanganate in an all-glass still.

¹ Smith, R. H., and Wilson, I. R., *Aust. J. Chem.*, 1966, **19**, 1357, 1365; 1967, **20**, 1353.

² Bridgart, G. J., and Wilson, I. R., *Aust. J. Chem.*, 1971, **24**, 2481.

³ Bridgart, G. J., and Wilson, I. R., *Aust. J. Chem.*, 1971, **24**, 2695.

⁴ Jones, G. D., and Zimmerman, R. L., U.S. Pat. 2,757,190 (1956).

⁵ Johar, G. S., Agarwala, U., and Rao, P. B., *Indian J. Chem.*, 1970, **8**, 759.

⁶ Vogel, A. I., 'A Textbook of Quantitative Inorganic Analysis' 3rd Edn, p. 433 (Longmans: London 1962).

Kinetic Measurements

Reaction mixtures were prepared from stock solutions of peroxomonosulphate, sulphuric acid and alkyl isothiocyanate with redistilled water.

The alkyl isothiocyanate stock solutions were prepared fresh daily from known weights of the pure liquids. The solutions of methyl isothiocyanate all contained $c. 10^{-3}$ M edta to prevent the previously recorded metal-ion catalysed decomposition of methyl isothiocyanate in aqueous solution³ although no evidence was found for a similar reaction involving ethyl isothiocyanate. It was confirmed that this amount of added edta had no effect on the analytical method for peroxomonosulphate. An ethyl isothiocyanate/peroxomonosulphate reaction containing edta at this level showed no significant difference from corresponding reactions without edta added. All kinetic results were obtained by sampling the reaction mixture and analysing for peroxomonosulphate by the standard arsenious acid method.¹ The temperature of all reaction mixtures was controlled to be $25.0 \pm 0.1^\circ\text{C}$.

Results

The stoichiometry of the reaction was determined by analysis of mixtures containing alkyl isothiocyanate and an excess of peroxomonosulphate. After several hours, the oxidant was found to have been consumed in amounts between 2.9_0 and 3.0_2 mol per 1 mol of isothiocyanate originally present. A stoichiometry of 3 : 1 is thus indicated. The only comparison to this result is to be found in a paper⁷ dealing with α -thiocyanato and α -isothiocyanato sulphides. The oxidation of methyl isothiocyanate by peroxophthalic acid in ether solution is there reported to only consume two moles of oxidant, but several alkyl α -isothiocyanato sulphides consume three moles of this oxidant more than the corresponding isomeric α -thiocyanato sulphide. The authors do not interpret this result.

By integrated rate studies, the rate law was found to be of the form

$$d[\text{HOOSO}_3^-]/dt = -k[\text{HOOSO}_3^-][\text{RNCS}] \quad (1)$$

with little dependence of rate on (sulphuric) acid concentration. Integration of the above, assuming the 3 : 1 stoichiometry, gives

$$[3/(a-3b)] \ln[3bx/a(x+3b-a)] = kt$$

where $x = [\text{HOOSO}_3^-]$, $a = [\text{HOOSO}_3^-]_0$ and $b = [\text{RNCS}]_0$, and Fig. 1 gives a typical plot of this function. Linearity is good throughout the reaction, in this case the five points corresponding to 42, 66, 82, 91 and 96% of complete reaction. Values of the rate constant k (measured as the slope of graphs similar to Fig. 1) for a selection of experiments at 25.0°C made with different initial conditions are given in Table 1.

Measurements of initial rates confirmed the rate law (1), and gave values for the rate constants in good agreement with those quoted above. Thus it is established that the 3 : 1 mole ratio applies throughout the reaction and the reaction rate is controlled by an initial (second-order) reaction with subsequent rapid consumption of a further two moles of oxidant.

The usual product from peroxomonosulphate in its oxidation reactions is, of course, sulphate. A standard gravimetric sulphate analysis, using lead(II) as the precipitating cation, gave the result that a mixture originally containing 2.10×10^{-3} mol of HOOSO_3^- , 3.04×10^{-3} mol of H_2SO_4 and 2.30×10^{-3} mol of EtNCS eventually contained 5.12×10^{-3} mol of sulphate after the reaction was complete. Thus, all of the HOOSO_3^- is converted quantitatively into sulphate. In addition, the standard

⁷ Böhme, H., and Scheel, U., *Chem. Ber.*, 1967, **100**, 347.

arsenate analyses for peroxomonosulphate showed that no significant amounts of hydrogen peroxide are formed during the reaction.

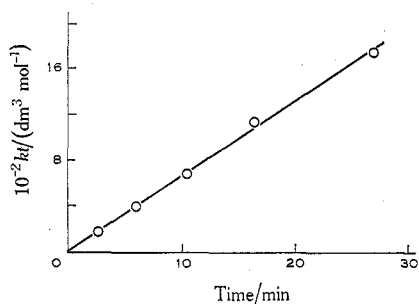


Fig. 1. Integrated rate plot for oxidation of methyl isothiocyanate by peroxomonosulphuric acid.

Initial concentrations:

$[\text{HOOSO}_3^-]$ $0.0106 \text{ mol dm}^{-3}$;

$10^3[\text{MeNCS}]$ 1.9 mol dm^{-3} .

Table 1. Rate constants (k) for the oxidation of alkyl isothiocyanates by peroxomonosulphuric acid
Temperature 25.0°C . Concentrations in mol dm^{-3} , k in $\text{dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

Methyl isothiocyanate				Ethyl isothiocyanate			
$[\text{HOOSO}_3^-]_0$	$[\text{MeNCS}]_0$	$[\text{H}^+]$	k	$[\text{HOOSO}_3^-]_0$	$[\text{EtNCS}]_0$	$[\text{H}^+]$	k
10.6×10^{-3}	3.8×10^{-3}	0.44	0.97	10.6×10^{-3}	3.4×10^{-3}	0.44	0.73
10.6×10^{-3}	1.9×10^{-3}	0.44	1.02	10.6×10^{-3}	1.7×10^{-3}	0.44	0.79
10.6×10^{-3}	3.8×10^{-3}	0.83	1.03	5.3×10^{-3}	1.7×10^{-3}	0.42	0.77
5.3×10^{-3}	1.9×10^{-3}	0.42	1.14	17.4×10^{-3}	4.8×10^{-3}	0.86	0.75 ^B
10.6×10^{-3}	1.9×10^{-3}	0.44	1.10^A				

^A Mean $1.05 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$.

^B Mean $0.75 \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$.

The eventual product from the alkyl isothiocyanate has proved more difficult to identify. The sulphur is not converted into sulphate. It was established that neither elemental sulphur nor ionic sulphide, nor indeed sulphite are products. The failure of a (*verified*) colorimetric technique⁸ showed that the isothiocyanate does not split on oxidation to yield a nitroalkane, and the obvious conclusion is that the final oxidation product retains the nitrogen and sulphur from the isothiocyanate. Repeated attempts at solvent extraction to isolate the product were unsuccessful, and this leads us to suggest that this product has high solubility in water. It could, for example, be a sulphonate species like RNHCOSO_3^- .

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⁸ Ashworth, M. R. F., and Gransch, E., *Mikrochim. Acta*, 1967, 358.