Fitting of kinetic data

4-bromodimethylaniline

The solid black line is the fitted curve and the coloured curve the absorbance data. Absorbance data was fitted to a single exponential term. All graphs show absorbance on the ordinate and time (in seconds) on the abscissa. The borate concentration is indicated by the label on the ordinate axis.
dimethylaniline

The solid black line is the fitted curve and the coloured curve the absorbance data. Absorbance data was fitted to a single exponential term. All graphs show absorbance on the ordinate and time (in seconds) on the abscissa. The borate concentration is indicated by the label on the ordinate axis.
**p-methyldimethylaniline**

The solid black line is the fitted curve and the coloured curve the absorbance data. Absorbance data was fitted to a single exponential term. All graphs show absorbance on the ordinate and time (in seconds) on the abscissa. The borate concentration is indicated by the label on the ordinate axis.
p-aminoldimethylaniline

The solid black line is the fitted curve and the coloured curve the absorbance data. Absorbance data was fitted to a double exponential term. All graphs show absorbance on the ordinate and time (in seconds) on the abscissa. The borate concentration is indicated by the label on the ordinate axis.

Variable | Value    | Std. Err.
--- | --- | ---
$k_1$  | 4.677e-004 | 3.789e-006
$A_1$  | 1.730e-001 | 8.513e-004
$A_{\infty}$  | 9.356e-001 | 1.219e-003
$k_2$  | 4.779e-005 | 2.187e-007
$A_2$  | 6.777e-001 | 5.516e-004

Variable | Value    | Std. Err.
--- | --- | ---
$k_1$  | 4.805e-004 | 3.740e-006
$A_1$  | 1.974e-001 | 9.179e-004
$A_{\infty}$  | 8.658e-001 | 1.183e-003
$k_2$  | 5.023e-005 | 2.039e-007
$A_2$  | 7.706e-001 | 5.249e-004

Variable | Value    | Std. Err.
--- | --- | ---
$k_1$  | 4.652e-004 | 3.584e-006
$A_1$  | 2.071e-001 | 1.013e-003
$A_{\infty}$  | 8.584e-001 | 1.009e-003
$k_2$  | 5.507e-005 | 2.053e-007
$A_2$  | 7.894e-001 | 4.898e-004
Thiocyanate

The solid black line is the fitted curve and the coloured curve the absorbance data. Absorbance data was fitted to a single exponential term. All graphs show absorbance on the ordinate and time (in seconds) on the abscissa. The borate concentration is indicated by the label on the ordinate axis.
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Log plot for the reaction of iodide with hydrogen peroxide in the presence of a range of borate concentrations. Iodide was in excess and the reaction was followed by removing 0.1ml aliquots of reaction solution and adding to 2ml titanium (IV) sulfate in sulfuric acid; the absorbance was measured at 410nm. Reaction conditions were: \([I^-] = 0.02M; [H_2O_2] = 0.00416M; [Borate], as shown in key; I = 0.5M with sodium sulfate; pH 9.84.

Log plot for the reaction of bromide with hydrogen peroxide in the presence of a range of borate concentrations. Bromide was in excess and the reaction was followed by removing 0.1ml aliquots of reaction solution and adding to 2ml titanium (IV) sulfate in sulfuric acid; the absorbance was measured at 410nm. Reaction conditions were: \([Br^-] = 0.2M; [H_2O_2] = 0.0416M; [Borate], as shown in key; I = 0.5M with sodium sulfate; pH 9.79.
**NH₂NH₂**

Log plot for the reaction of hydrazine with hydrogen peroxide in the presence of a range of borate concentrations. Hydrazine was in excess and the reaction was followed by removing 0.1ml aliquots of reaction solution and adding to 2ml titanium (IV) sulfate in sulfuric acid; the absorbance was measured at 410nm. Reaction conditions were: [Hydrazine] = 0.114M; [H₂O₂] = 0.0416M; [Borate], as shown in key; I = 0.5M with sodium sulfate; pH 9.78.

![Log plot for the reaction of hydrazine with hydrogen peroxide in the presence of a range of borate concentrations.](image)

**4-bromophenylmethyl sulfoxide**

Plots for the reaction of bromophenylmethyl sulfoxide with hydrogen peroxide in the presence and absence of borate. Absorbance changes were followed at 248nm having first removed the hydrogen peroxide from solution using bovine catalase (pH adjusted using HCl or NaOH prior to catalase addition). Conditions were: [sulfoxide] = 7.8x10⁻⁵ M; [H₂O₂] = 0.416M; pH as indicated in key; I = 0.111. Low pH experiments were carried out in a 0.1M acetate buffer.

![Plots for the reaction of bromophenylmethyl sulfoxide with hydrogen peroxide in the presence and absence of borate.](image)
Methyl-p-tolyl sulfoxide

Plots for the reaction of methyl-p-tolyl sulfoxide with hydrogen peroxide in the presence and absence of borate. Absorbance changes were followed at 240nm having first removed the hydrogen peroxide from solution using bovine catalase (pH adjusted using HCl or NaOH prior to catalase addition). Conditions were: [sulfoxide] = 9.14x10^-5 M; [H₂O₂] = 0.416M; pH as indicated in key; I = 0.111. Low pH experiments were carried out in a 0.1M acetate buffer.
Calculated geometries of reactants, transition states and products

1. Me₂S

2. HS⁻

3. I⁻
10. \( p\text{-MeC}_6H_4S(\text{O})\text{Me} \)

11. SCN\(^-\)

**Colour coding:**
- H, cyan
- B, green
- C, grey
- N, blue
- O, red
- S, yellow
- Br, orange
- I, violet.