Table 10

Kinetic data for the reaction of 4-nitrobenzofurazan[a] with nitroethane and methoxide in methanol at 25°C.

[Nitroethane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]^b$eq/ 10^{-4} mol dm^{-3}	$[MeCHNO_2^-]^b$eq/ 10^{-3} mol dm^{-3}	$k_{fast}{}^d/s^{-1}$	Ampt	$K_5{}^e$/ 10^4 dm^3 mol^{-1}
0.025	0.5	0.4	0.5	0.054	0.52	-
0.050	2.5	1.0	2.4	0.20	0.63	-
0.025	5.0	4.0	4.6	0.38	0.62	-
0.050	5.0	2.0	4.8	0.38	0.63	-
0.100	5.0	1.0	4.9	0.42	0.64	-
0.0010	5.0	0.54[c]	0.027	0.0025	0.40	6.4
0.0015	5.0	0.54[c]	0.040	0.0031	0.45	6.3
0.0020	5.0	0.54[c]	0.054	0.0037	0.49	6.5

Table 10 (continued)

				$k^{f}slow/10^{-4}$ s^{-1}
0.167	0.020	3.0	0.020	4.0
0.117	0.020	4.0	0.020	6.0
0.083	0.020	6.0	0.020	8.0
0.050	0.020	13.0	0.020	20

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated using a value for K_{CH} of 500 dm^3 mol^{-1}.

c. Equilibrium methoxide concentration in bromophenol buffers.

d. Measured as a colour forming process at 335 nm.

e. Calculated as Ampt/(0.63-Ampt)·$(MeCHNO_2^-)$eq.

f. Measured as a forming process at 370 nm.

Table 11

Kinetic data for the reaction of 4-nitrobenzofurazan[a] with 2-nitropropane and methoxide in methanol at 25°C.

[2-Nitropropane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]^b$eq/ 10^{-5} mol dm^{-3}	$[Me_2CNO_2^-]^b$/ 10^{-3} mol dm^{-3}	k^c_{fast}/s^{-1}
0.050	0.50	0.39	0.50	0.0043
0.050	1.25	0.96	1.23	0.0063
0.050	2.50	1.92	2.50	0.0098
0.050	3.75	2.88	3.74	0.0134
0.050	5.0	3.80	4.94	0.0157
0.025	5.0	7.70	5.00	0.0152

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated using a value for K_{CH} of 2600 dm^3 mol^{-1}.

c. Measured as a colour forming process at 335 nm.

Table 12

Kinetic data for the reaction of 7-methoxy-4-nitrobenzofurazan[a] with nitromethane and methoxide in methanol at 25ºC

[Nitromethane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]_{eq}$[b]/ 10^{-4} mol dm^{-3}	$[CH_2NO_2^-]_{eq}$[b]/ 10^{-3} mol dm^{-3}	k_{fast}[d]/s^{-1}
0.15	0.50	1.2	0.40	0.046
0.15	1.0	2.4	0.80	0.079
0.15	1.5	3.6	1.1	0.117
0.15	2.0	4.8	1.5	0.149
0.15	2.5	6.0	1.9	0.184
0.30	2.5	3.3	2.2	0.188
0.0010	5.0[c]	0.54	0.0011	0.0026
0.0015	5.0[c]	0.54	0.0017	0.0027
0.0020	5.0[c]	0.54	0.0023	0.0029

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated using a value for K_{CH} of 21 dm^3 mol^{-1}.

c. Equilibrium methoxide concentration in bromophenol buffers.

d. Measured as a fading process at 375 nm.

Table 13

Kinetic data for the reaction of 7-methoxy-4-nitrobenzofurazan[a] with nitroethane and methoxide in methanol at 25ºC.

[Nitromethane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]_{eq}$[b]/ 10^{-4} mol dm^{-3}	$[MeCHNO_2^-]_{eq}$[b]/ 10^{-3} mol dm^{-3}	k_{fast}/s^{-1}
0.10	1.0	0.20	0.98	0.030
0.10	1.5	0.30	1.47	0.040
0.050	4.0	0.80	1.92	0.060
0.10	3.0	0.60	2.94	0.090
0.10	4.0	0.81	3.92	0.12
0.10	5.0	1.0	4.90	0.15
0.0010	5.0[c]	0.54	0.027	0.0021
0.0015	5.0[c]	0.54	0.040	0.0022
0.0020	5.0[c]	0.54	0.054	0.0022

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated using a value of K_{CH} of 500 dm^3 mol^{-1}.

c. Equilibrium concentration in bromophenol buffers.

d. Measured as a fading process at 375 nm.

Table 14

Kinetic data for the reaction of 7-methoxy-4-nitrobenzofurazan[a] with 2-nitropropane and methoxide in methanol at 25ºC

[2-Nitropropane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]_{eq}$[b]/ 10^{-4} mol dm^{-3}	$[Me_2CNO_2^-]$[b]/ 10^{-2} mol dm^{-3}	k_{fast}[c]/s^{-1}
0.050	5.0	0.38	0.49	0.022
0.050	10.0	0.77	0.99	0.028
0.050	15.0	1.15	1.49	0.034
0.050	20.0	1.54	1.98	0.039
0.050	30.0	2.31	2.98	0.052

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated using a value of K_{CH} of 2600 dm^3 mol^{-1}.

c. Measured as a fading process at 375 nm.

Table 15

Kinetic data for the reaction of 7-chloro-4-nitrobenzofurazan[a] with 2-nitropropane and methoxide in methanol at 25ºC.

[2-Nitropropane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]_{eq}$[b]/ 10^{-5} mol dm^{-3}	$[Me_2CNO_2^-]_{eq}$[b]/ 10^{-3} mol dm^{-3}	k_{fast}[c]/s^{-1}
0.031	0.5	0.61	0.49	0.011
0.031	1.0	1.23	0.99	0.016
0.031	1.5	1.85	1.80	0.022
0.031	2.0	2.46	1.99	0.026
0.031	2.5	3.10	2.50	0.033
0.063	2.5	1.54	2.50	0.034

a. Concentration is 5×10^{-5} mol dm^{-3}.

b. Calculated with a value for K_{CH} of 2600 dm^3 mol^{-1}

c. Colour forming reaction 320-350 nm.

Kinetics of the reaction of 7-chloro-4-nitrobenzofurazan, **2b**, with nitromethane and methoxide in methanol at 25ºC.

The reactions to be considered are:

$$\mathbf{2b} + CH_2NO_2^- \xrightarrow{k_5} \mathbf{6b} \text{ (carbanion adduct)}$$

$$\mathbf{2b} + MeO^- \underset{k_{-OMe}}{\overset{k_{OMe}}{\rightleftharpoons}} \text{5-MeO adduct}$$

The formation of **6b** will be essentially irreversible with a low value for the reverse rate constant. The methoxide addition has been reported[21] to have values of k_{OMe} 5100 $dm^3\ mol^{-1}\ s^{-1}$ and k_{-OMe} 1.8 s^{-1}. Since the concentrations of carbanion and methoxide do not change in any one kinetic run first order kinetics are observed. A semi-quantitative kinetic treatment following the methods of Bernasconi[35] gave the equation (3).

$$k_{fast} = k_5[CH_2NO_2^-] + k_{OMe}[MeO^-] + k_{-OMe}\left(\frac{k_{OMe}[MeO^-]}{k_{OMe}[MeO^-] + k_5[CH_2NO_2^-]}\right) \qquad (3)$$

Table 16

[Nitromethane]/ mol dm^{-3}	[NaOMe]/ 10^{-3} mol dm^{-3}	$[MeO^-]_{eq}$[a]/ 10^{-4} mol dm^{-3}	$[CH_2NO_2^-]_{eq}$[a]/ 10^{-3} mol dm^{-3}	k_{fast}[b]/s^{-1}	k_{calc}[c]/s^{-1}
0.15	1.0	2.4	0.80	3.56	3.47
0.15	1.5	3.6	1.14	4.90	4.70
0.15	2.0	4.8	1.52	6.01	5.90
0.15	2.5	6.0	1.90	6.98	7.08
0.05	2.5	12.4	1.26	9.73	10.02
0.30	2.5	3.5	2.15	5.93	5.81
0.45	2.5	2.4	2.26	4.80	5.22

a. Calculated with K_{CH} 21 dm^3 mol^{-1}.

b. Colour forming reaction at 320 nm.

c. Calculated with k_5 1500 dm^3 mol^{-1} s^{-1}, k_{OMe} 5300 dm^3 mol^{-1} s^{-1} and k_{-OMe} 2.0 s^{-1}. These are the optimised values to give the best fit with the given equation (3).