SUPPLEMENTARY MATERIAL

Table S.1: Second order rate constants, k^{Ox}, for nucleophilic substitution of sarin and soman, as derived from a potentiometric monitoring of the reactions in the presence of an external buffer.[a,b]

Oxime	pK_a^{Ox}	$[Ox]_0$, mol dm^{-3}	External Buffer	k^{Ox}, dm^3 mol^{-1} s^{-1}	
				Sarin	Soman
1a	6.54	2x10^{-3}	HEPES	0.31	-
		4x10^{-3}	HEPES	0.33	0.14
2	6.98	2x10^{-3}	HEPES	-	0.25
3	7.13	2x10^{-3}	HEPES	1.52	0.40
		4x10^{-3}	HEPES	1.43	0.45
7	7.75	2x10^{-3}	HEPES	4.70	1.45
		4x10^{-3}	HEPES	4.86	1.40
		8x10^{-3}	HEPES	4.69	-
8	8.05	2x10^{-3}	HEPES	8.00	2.25
		2x10^{-3}	TAPS	8.10	2.15
		4x10^{-3}	HEPES	8.04	-
9	8.27	2x10^{-3}	HEPES	6.45	-
1.d	8.30	4x10^{-3}	TAPS	5.05	1.90
		4x10^{-3}	HEPES	4.90	-
11	9.30	6x10^{-3}	TAPS	8.90	4.30
		8x10^{-3}	TAPS	8.70	4.40
12	9.55	6x10^{-3}	TAPS	13.40	5.34
		8x10^{-3}	TAPS	13.52	5.82
13	9.85	6x10^{-3}	TAPS	-	5.30
		8x10^{-3}	TAPS	14.70	5.70
14	9.95	6x10^{-3}	TAPS	13.10	-

(a) Total HEPES or TAPS concentration of 0.10 mol dm^{-3}; 1:1 HEPES (pH=7.49) or TAPS (pH=8.30) buffers; [sarin] or [soman] = 10^{-3} mol dm^{-3}; (b) see ref. 41 for the complete description of the potentiometric methodology.

Figure S1: Plots illustrating the dependence of k_{obs} on the oximate concentration at constant pH and T=25°C for the phosphonate BNPPP; upper line: 2,3-butandionemonoxime 1:1 buffers (**11**, pH=9.30); lower line, $CH_3SCH_2COCH=NOH$ 1:1 buffers (**1c,** pH=8.16) in aqueous solution; I = 0.1 mol dm^{-3} KCl.

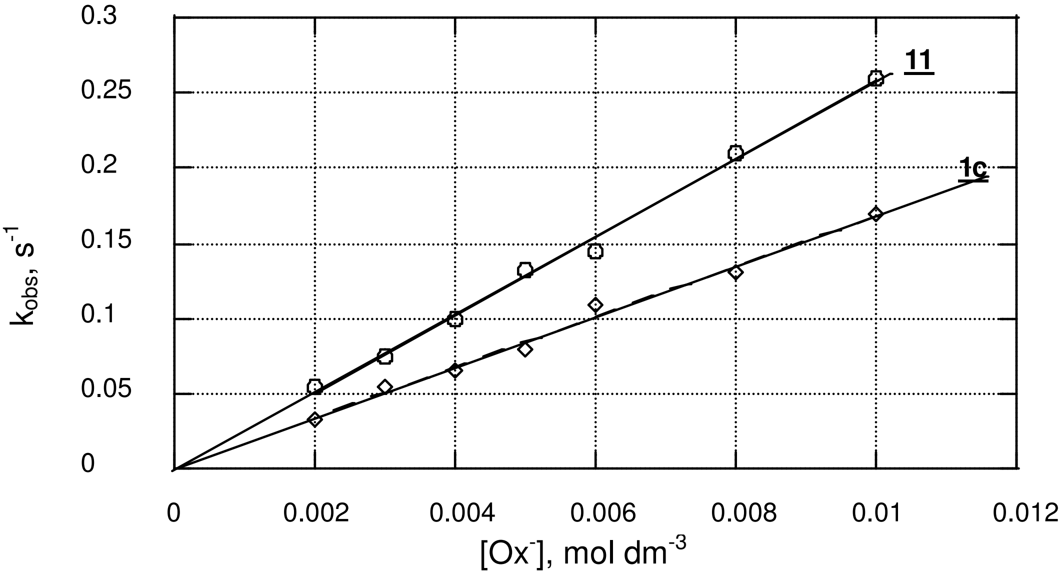

Figure S2: Plot illustrating the dependence of k_{obs} on the oximate concentration at constant pH for the phosphonate BNPMP in 2-pyridiniumaldoximate 1:1 buffers (7, pH = 9.00) at 25°C in 30:70 (v/v) H_2O-Me_2SO.

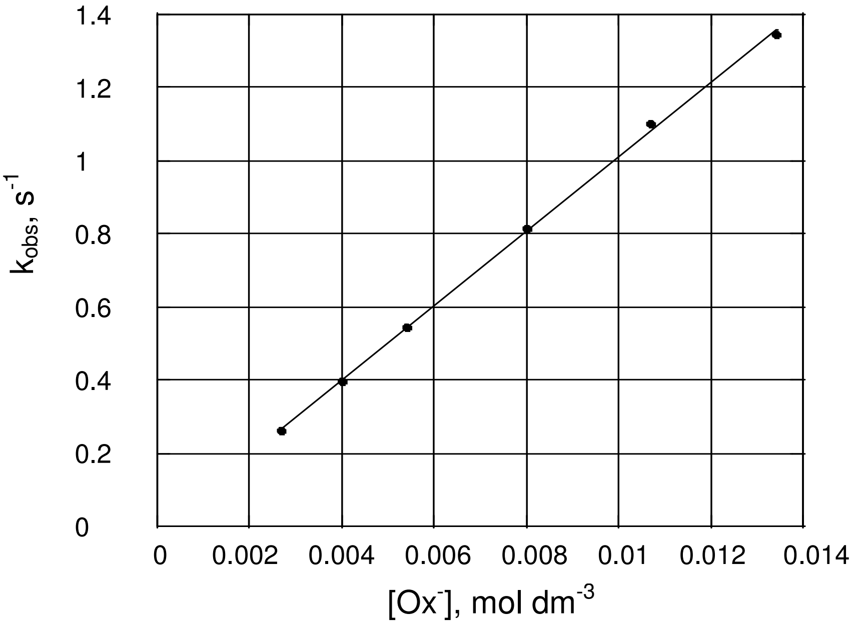

Figure S3: Plot illustrating the dependence of k_{obs} on the oximate concentration at constant pH for the phosphonate BNPPP reacting in 2-pyridinealdoximate 1:1 buffers (**<u>13</u>** , pH = 9.85) at 25°C in aqueous solution. For avoiding overlap with substitution of the second *p*-nitrophenoxide group of BNPPP, the k_{obs} values were determined by monitoring the first substitution up to 50% release of the first mole of this anion.

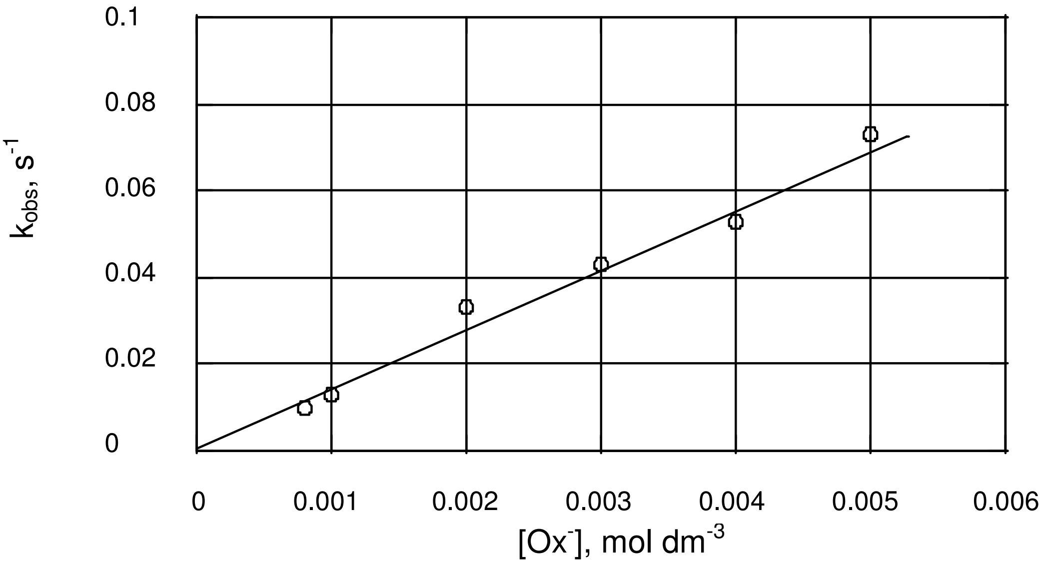

Figure S4: Oscilloscope trace illustrating the first order decomposition of soman by the 2-pyridiniumaldoxime 7 at pH = 7.49 in a 1:1 HEPES buffer, as derived from a potentiometric monitoring of the resulting increase in the F$^-$ concentration. See text.

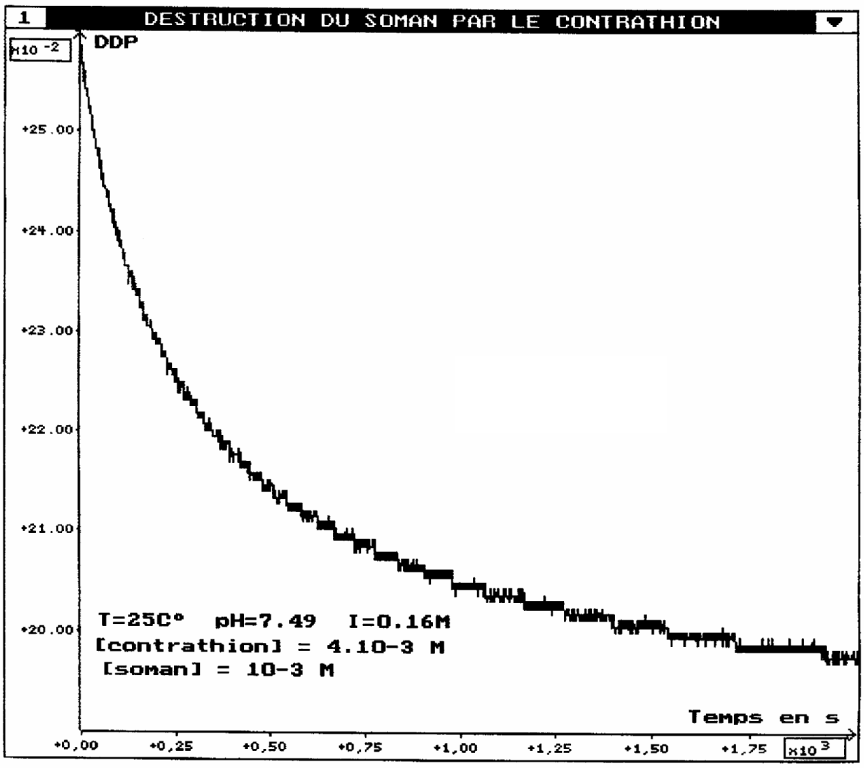

Figure S5 : Graph according to eq. (7) illustrating the decomposition of DFP in an external HEPES buffer containing a total pyridinium aldoxime (<u>7</u>) concentration of $4x10^{-3}$ mol dm^{-3} (pH = 7.49; T = 25°C).

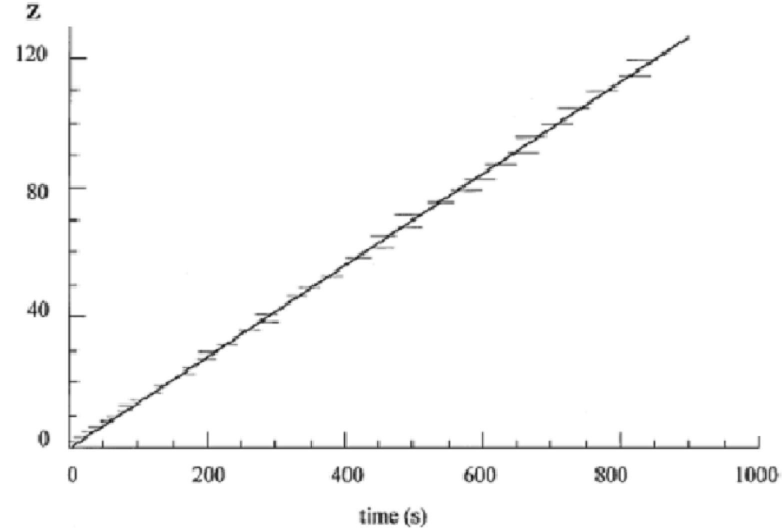

Figure S6: Effect of the oximate concentration on the observed first-order rate constant, k_{obs}, as measured potentiometrically for the decomposition of DFP in HI-6 buffers (**3**, pH=7.13) at 25°C in aqueous solution.