Electronic Supplementary Information for Dalton Transactions

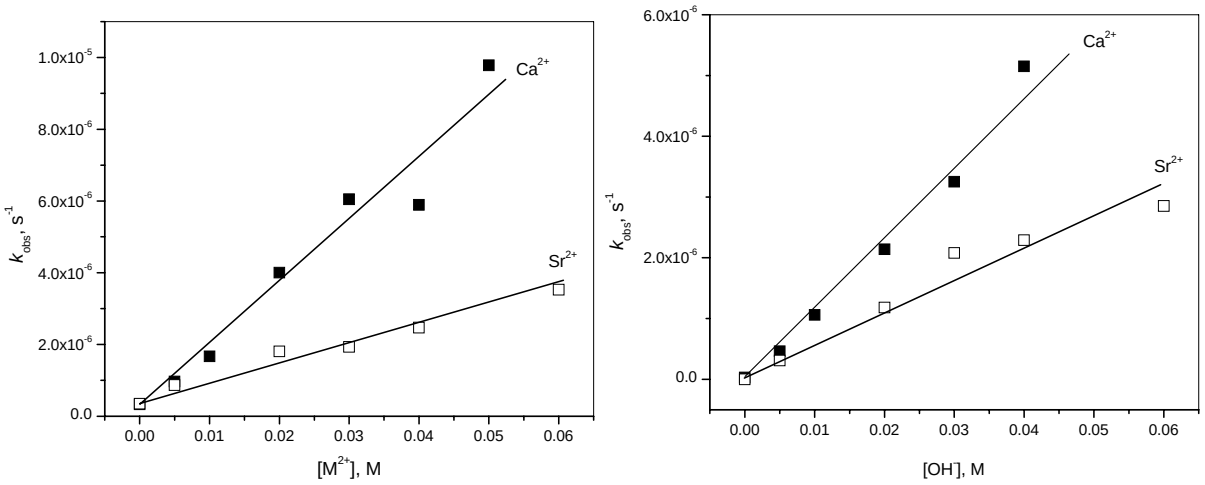
Supplementary Information

Rapid hydrolysis of model phosphate diesters by alkaline earth cations in aqueous DMSO: speciation and kinetics

Olga Taran, [a] Felipe Medrano [b] and Anatoly K. Yatsimirsky * [a]

[a] *Facultad de Química, Universidad Nacional Autónoma de México, 04510 México D.F., México. E-mail: anatoli@servidor.unam.mx*

[b] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, 62209; Cuernavaca, Morelos, México.*



A B

Fig. S1. Kinetics of BNPP hydrolysis in the presence of Ca^{2+} and Sr^{2+} in water at variable metal ion and hydroxide concentrations at 37°C. (A) Variable metal in the presence of 10 mM NaOH (B) Variable NaOH in the presence of 5 mM metal ion.

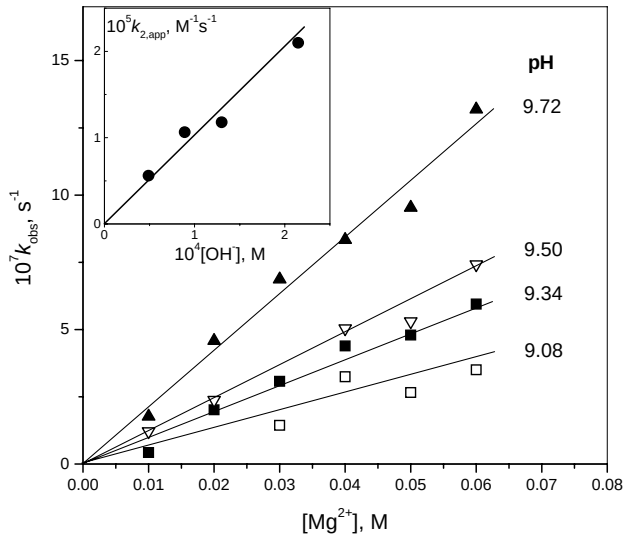


Fig. S2. Kinetics of BNPP hydrolysis in the presence of Mg^{2+} at variable metal ion concentration and pH in 0.05 M TRIS at 37°C. Inset: plot of the observed second-order rate constant vs. concentration of free hydroxo ions. The linearity of plots at each given pH value confirms the first order kinetics in Mg(II) and the slopes of these plots ($k_{2,app}$) are directly proportional to concentrations of hydroxide ions corresponding to each pH value (see inset).

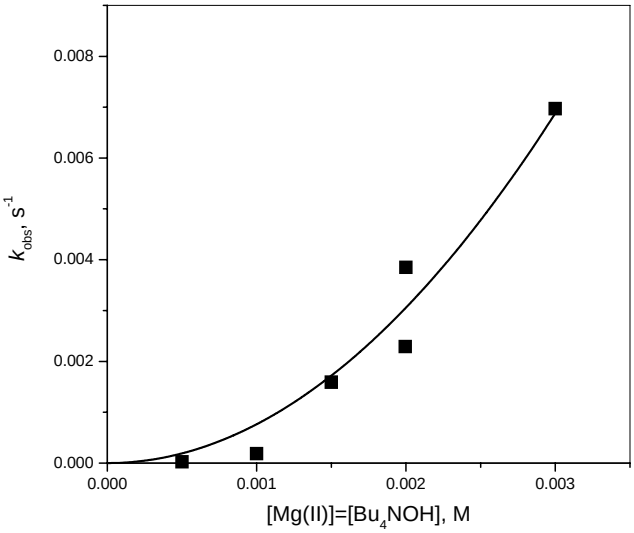


Fig. S3. Observed first-order rate constants for BNPP cleavage in 90 % DMSO measured at variable concentration of $Mg(ClO_4)_2$ in the presence of 1 mol equivalent of Bu_4NOH.

Table S1. Results of potentiometric titrations of alkaline earth cations in 90% vol DMSO.

The mean values of $\log\beta_{pq}$ are given with standard errors. Fitting errors in $\log\beta_{pq}$ calculated by Hyperquad in each titration experiment were less than 0.05. Goodness of fit is measured in Hyperquad by *sigma*, the value of the scaled sum of squares, which is given in the table together with $\log\beta_{pq}$ values for each titration.

		$\log\beta_{pq}$			
$[Mg(ClO_4)_2]$, mM	**sigma**	**1 -1**	**1 -2**	**2 -5**	**1 -3**
0.6	14.08	-11.50	-22.41	-58.34	-39.32
1.0	2.51	-11.49	-22.98	-60.40	-41.23
1.13	2.93	-11.46	-22.48	-60.23	-40.59
2.23	4.84		-22.30	-58.90	-41.10
mean		**-11.48±0.01**	**-22.5±0.2**	**-59.5±0.4**	**-40.6±0.4**
$[Ca(ClO_4)_2]$, mM	**sigma**	**2 -1**	**1 -1**	**1 -2**	**2 -5**
0.53	2.15	-7.49	-11.71	-26.10	-67.50
1.0	1.35	-8.42	-12.70	-26.70	-66.10
1.0	2.51	-8.10	-11.85	-26.10	-66.65
1.02	59.86	-8.42	-12.54	-26.20	-67.90
1.93	14.60	-9.00	-12.53	-26.40	-69.50
mean		**-8.3±0.2**	**-12.3±0.2**	**-26.3±0.1**	**-67.5±0.6**
$[Sr(ClO_4)_2]$, mM	**sigma**	**2 -1**	**1 -1**	**2 -5**	
0.5	1.78	-7.92	-12.76	-73.85	
1.0	1.63	-8.40	-13.87	-77.02	
1.93	14.28	-10.38	-14.00	-75.10	
mean		**-8.9±0.8**	**-13.5±0.4**	**-75.3±0.9**	

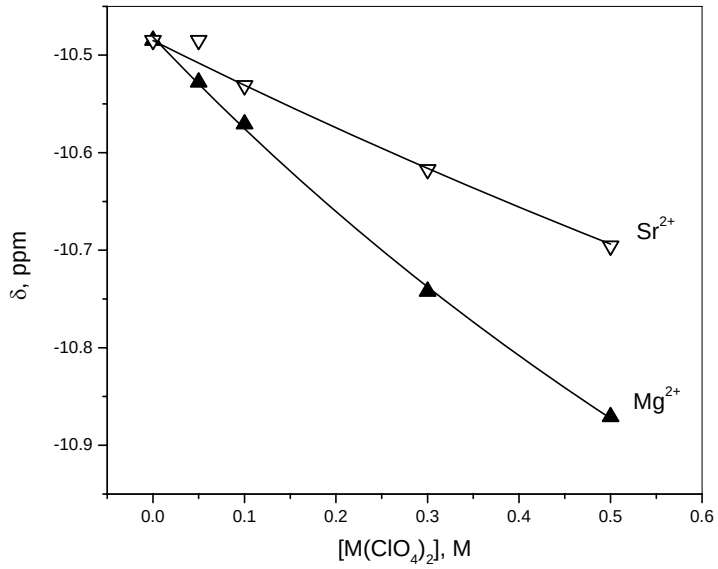


Fig. S4. ^{31}P NMR shifts of 5 mM BNPP at variable concentrations of Mg(II) and Sr(II) perchlorates in D_2O at 37°C. Solid lines are best fits to the theoretical equation (S1).

$$\delta_{obs} = (\delta_S + \delta_{MS}K_S[M(II)])/(1 + K_S[M(II)]) \qquad (S1)$$

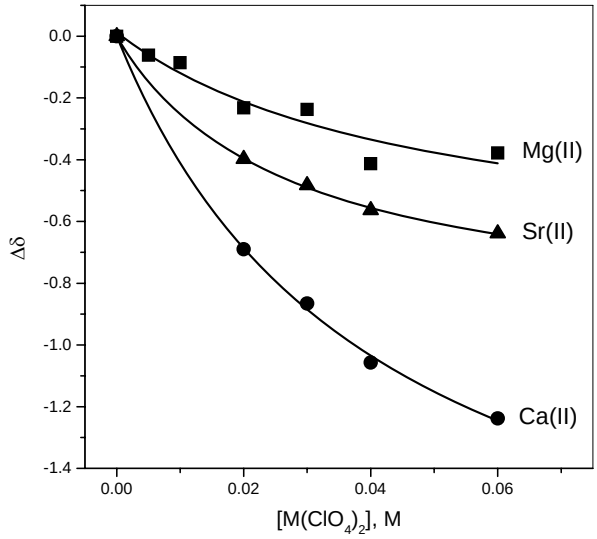


Fig. S5. ^{31}P NMR titrations of 5 mM BNPP by metal perchlorates in 90% DMSO/D_2O at 37°C. Solid lines are best fits to the theoretical equation (S1).

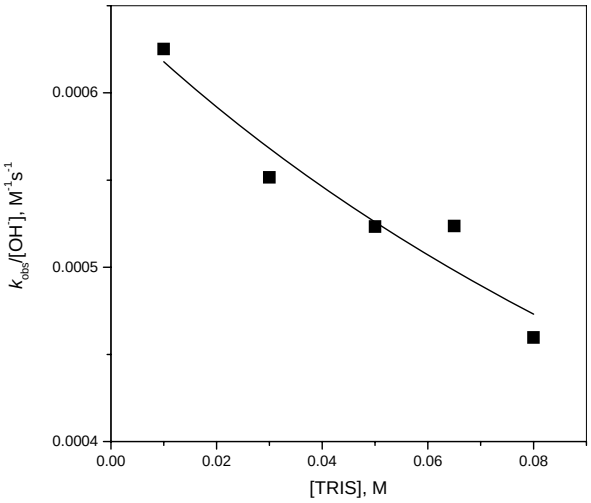


Fig. S6. Kinetics of BNPP hydrolysis in the presence of 5 mM Mg^{2+} at variable TRIS concentration and pH 9.0 at 37°C.