

# Zinc<sup>2+</sup>-Catalyzed Methanolysis of Phosphate Triesters: a Process for Catalytic Degradation of the Organophosphorus Pesticides Paraoxon and Fenitrothion.

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Supporting Information:

Part 1: Detailed analytical solution for the process proposed in Scheme 1.

Part 2: Detailed analytical solution for the process proposed in Scheme 2.

### Part 1: Detailed analytical solution for the process proposed in Scheme 1.

General assumptions are that we have two equilibrium constants and two equations for material balance.

Parameters defined as: OR = free methoxide ( $\text{OCH}_3$ ) ion;  $\text{Zn} = \text{Zn}^{2+}$ ;  $\text{ZnOR} = \text{Zn}^{2+}(\text{OCH}_3)$ ;  $\text{ZnORD} = \text{Zn}^{2+}(\text{OCH}_3)_2$ ;  $\text{Znt}$  is defined as the total concentration of  $\text{Zn}^{2+}$  from all sources, and  $\text{ORt}$  is defined as the total amount of methoxide ion from all sources.

Method: All equations generated using the program MAPLE 9 Release 9, Waterloo Maple Inc., Waterloo, Ontario, Canada. The format of the equations below is that directly obtained from MAPLE, red equations are the command lines and the blue equations are the solutions.

Equilibrium constants:

$$\begin{aligned} K1 &= \text{Zn} \cdot \text{OR} / \text{ZnOR}, \\ K2 &= \text{ZnOR} \cdot \text{OR} / \text{ZnORD}, \end{aligned}$$

Material balance under assumption that  $\text{OR} \ll \text{ORt}$  (under the experimental conditions where the pH is approximately 10 or less, the free OR  $\sim 10^{-7}\text{M}$  or less, while the total amount of added methoxide,  $\text{ORt} \sim 10^{-3}\text{M}$ )

$$\begin{aligned} \text{Znt} &= \text{Zn} + \text{ZnOR} + \text{ZnORD}, \\ \text{ORt} &= \text{ZnOR} + 2 \cdot \text{ZnORD} \end{aligned}$$

```
> solvefor[Zn] ( K1=Zn*OR/ZnOR, Znt=Zn+ZnOR+ZnORD/K2,
ORt=ZnOR + 2*ZnORD/K2 );
```

$$\left\{ \begin{aligned} \text{ORt} &= \frac{\text{ZnOR} (K2 + 2 \text{OR})}{K2}, \text{Zn} = - \frac{-\text{Znt} K2 + \text{ZnOR} K2 + \text{ZnOR} \text{OR}}{K2} \\ K1 &= - \frac{\text{OR} (-\text{Znt} K2 + \text{ZnOR} K2 + \text{ZnOR} \text{OR})}{\text{ZnOR} K2} \end{aligned} \right\}$$

Then we choose the first and third equation and solve them for OR:

```
> solvefor[OR] (K1 = -OR*(-Znt*K2+ZnOR*K2+ZnOR*OR) / (ZnOR*K2) ,
ORt = ZnOR*(K2+2*OR) / K2);
```

$$\left\{ \begin{aligned} K1 &= \frac{K2 (2 Znt ORt - 2 Znt ZnOR + ZnOR^2 - ORt^2)}{4 ZnOR^2} \\ OR &= \frac{K2 (ORt - ZnOR)}{2 ZnOR} \end{aligned} \right\}$$

We solve the above K1 equation for Znt:

```
> solvefor[Znt] (K1 = -1/4*(ORt*Kd-ZnOR*Kd)^(1/2)*(-
2*Znt+ZnOR+ORt)/ZnOR^2);
```

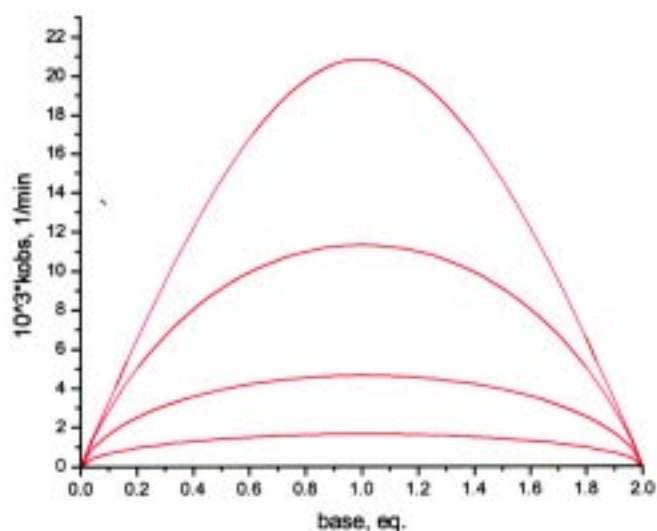
$$Znt = \frac{1}{2 \sqrt{ORt Kd - ZnOR Kd}} (4 K1 ZnOR^2 + \sqrt{ORt Kd - ZnOR Kd} ZnOR + \sqrt{ORt Kd - ZnOR Kd} ORt)$$

and isolate ZnOR from it:

```
> isolate(K1 = 1/4*K2*(2*Znt*ORt-2*Znt*ZnOR+ZnOR^2-
ORt^2)/ZnOR^2,ZnOR);
```

$$ZnOR = \frac{1}{2 (-K2 + 4 K1)} (-2 Znt K2 + 2 \sqrt{Znt^2 K2^2 - 2 Znt K2^2 ORt + K2^2 ORt^2 + 8 K1 Znt K2 ORt - 4 K1 K2 ORt^2})$$

This gives the expression for ZnOR, which when combined with the second-order catalytic rate constant  $k_{cat}$  of  $34 \text{ M}^{-1}\text{min}^{-1}$  (determined as discussed in section a. of the Discussion of the main paper) generated some possible dependencies of  $k_{obs}$  vs. [base] and  $k_{obs}$  vs.  $[Zn^{2+}]_{total}$ , which are shown as Figures 1S-8S, below.



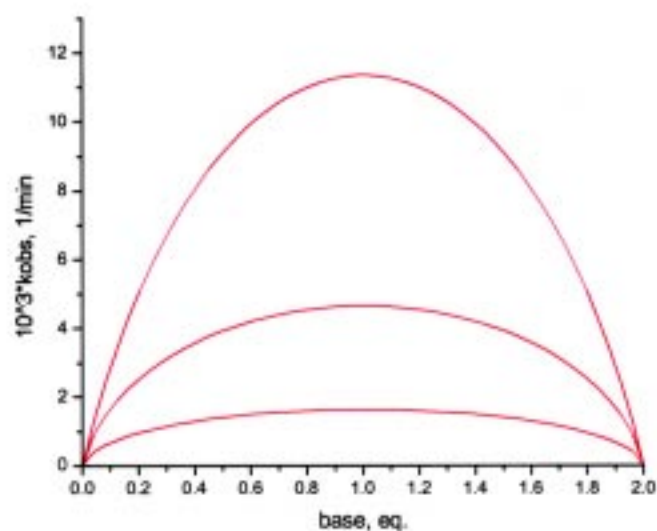
**Figure 1S, Computed plots of  $k_{\text{obs}}$  vs. added [methoxide], generated using the following parameters:**

$$K_1 = 10^{-6}; 10^{-7}, 10^{-8}, 10^{-9} \text{ mM}$$

$$K_2 = 10^{-8} \text{ mM}$$

$$[\text{Zn}]_{\text{total}} = 1 \text{ mM}$$

$$k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$$



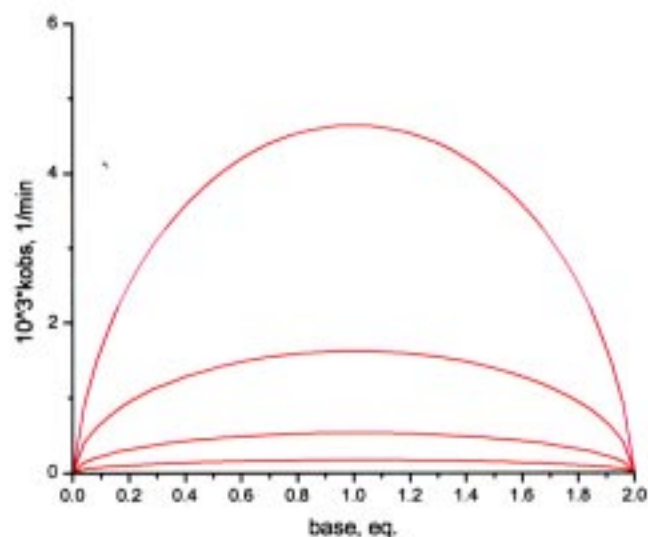
**Figure 2S, Computed plots of  $k_{\text{obs}}$  vs. added [methoxide], generated using the following parameters:**

$$K_1 = 10^{-3}; 10^{-4}, 10^{-5} \text{ mM}$$

$$K_2 = 10^{-5} \text{ mM}$$

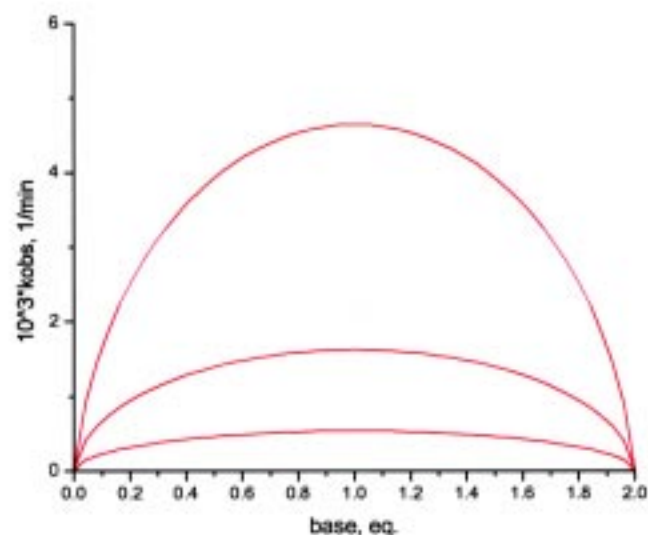
$$[\text{Zn}]_{\text{total}} = 1 \text{ mM}$$

$$k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$$



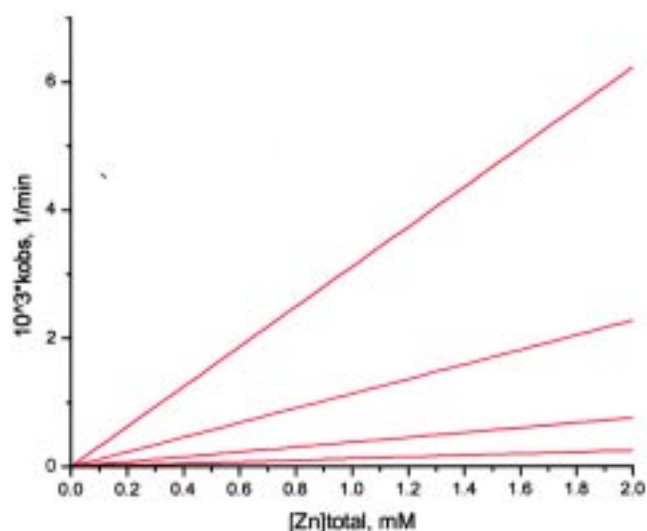
**Figure 3S, Computed plots of  $k_{\text{obs}}$  vs. added [methoxide], generated using the following parameters:**

$K_1 = 10^{-6} \text{ mM}$   
 $K_2 = 10^{-7}; 10^{-8}, 10^{-9}, 10^{-10} \text{ mM}$   
 $[\text{Zn}]_{\text{total}} = 1 \text{ mM}$   
 $k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$



**Figure 4S, Computed plots of  $k_{\text{obs}}$  vs. added [methoxide], generated using the following parameters:**

$K_1 = 10^{-4} \text{ mM}$   
 $K_2 = 10^{-5}; 10^{-5}, 10^{-7} \text{ mM}$   
 $[\text{Zn}]_{\text{total}} = 1 \text{ mM}$   
 $k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$



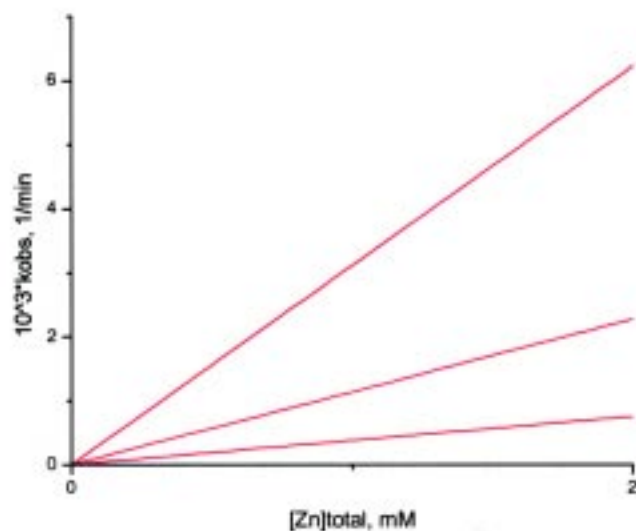
**Figure 5S, Computed plots of  $k_{obs}$  vs. added  $[Zn]_t$ , under conditions where the  $[OR]_t / [Zn]_t$  is held constant at 0.3 generated using the following parameters:**

$$K_1 = 10^{-6} \text{ mM}$$

$$K_2 = 10^{-7}; 10^{-8}, 10^{-9}, 10^{-10} \text{ mM}$$

$$[OR]_t / [Zn]_{total} = 0.3$$

$$k_{cat} = 34 \text{ M}^{-1} \text{ min}^{-1}$$



**Figure 6S, Computed plots of  $k_{obs}$  vs. added  $[Zn]_t$ , under conditions where the  $[OR]_t / [Zn]_t$  is held constant at 0.3 generated using the following parameters:**

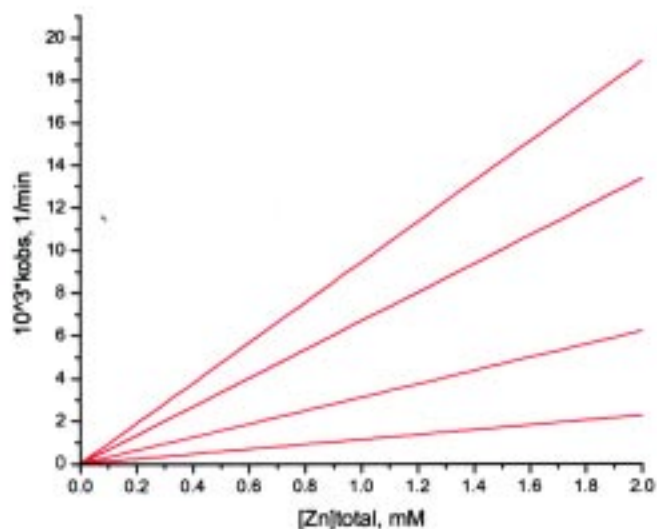
$$K_1 = 10^{-4} \text{ mM}$$

$$K_2 = 10^{-5}; 10^{-6}, 10^{-7} \text{ mM}$$

$$[OR]_t / [Zn]_{total} = 0.3$$

$$k_{cat} = 34 \text{ M}^{-1} \text{ min}^{-1}$$





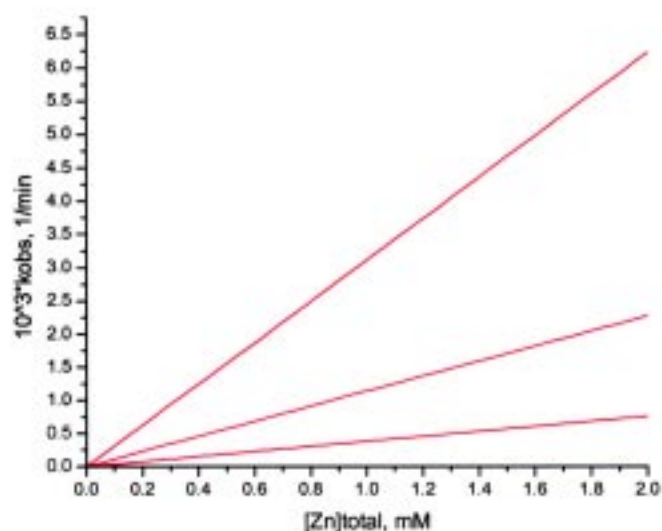
**Figure 7S, Computed plots of  $k_{\text{obs}}$  vs. added  $[\text{Zn}]_t$ , under conditions where the  $[\text{OR}]_t / [\text{Zn}]_t$  is held constant at 0.3 generated using the following parameters:**

$$K_1 = 10^{-6}; 10^{-7}, 10^{-8}, 10^{-9} \text{ mM}$$

$$K_2 = 10^{-8} \text{ mM}$$

$$[\text{OR}]_t / [\text{Zn}]_{\text{total}} = 0.3$$

$$k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$$



**Figure 8S, Computed plots of  $k_{\text{obs}}$  vs. added  $[\text{Zn}]_t$ , under conditions where the  $[\text{OR}]_t / [\text{Zn}]_t$  is held constant at 0.3 generated using the following parameters:**

$$K_1 = 10^{-3}; 10^{-4}, 10^{-5} \text{ mM}$$

$$K_2 = 10^{-6} \text{ mM}$$

$$[\text{OR}]_t / [\text{Zn}]_{\text{total}} = 0.3$$

$$k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$$

The net results of the above computations concerning analytical solutions to the species presented in Scheme 1 in all cases show that the maximum concentration of the ZnOR species, and therefore the maximum rate constant predicted using this scheme occurs at a  $[OR]_t/[Zn]_{total} = 1.0$ , and not at the observed experimental ratio which is 0.3. Also, the predicted dependency of the observed rate constant catalyzed by Zn<sub>t</sub> is, in all cases, strictly linear, contrary to what is observed experimentally. Thus, we conclude that Scheme 1 cannot explain the experimental data. Note that in all the above cases we have used values for K<sub>1</sub> and K<sub>2</sub> which vary about and encompass the known titration pK<sub>a1</sub> and pK<sub>a2</sub> values experimentally determined previously (10.66 and 8.94) (Gibson, G.; Neverov, A. A.; Brown, R. S. *Can. J. Chem.* **2003**, *81*, 495). Note also that the concentration of free methoxide can be considered as negligible, and thus neglected in the material balance at the  $\text{pH}$  values used in the experiment (always less than 10).

## Part 2. Detailed analytical solution for the process proposed in Scheme 2.

General assumptions are that we have two equilibrium constants and two equations for material balance.

Parameters defined as: OR = free methoxide ( $\text{OCH}_3$ ) ion;  $Zn = Zn^{2+}$ ;  $ZnOR = Zn^{2+}(\text{OCH}_3)$ ;  $ZnORD = (Zn^{2+}(\text{OCH}_3)_2)_2$ ;  $Zn_t$  is defined as the total concentration of  $Zn^{2+}$  from all sources, and  $OR_t$  is defined as the total amount of methoxide ion from all sources.

Method: All equations generated using the program MAPLE 9 Release 9, Waterloo Maple Inc., Waterloo, Ontario, Canada. The format of the equations below is that directly obtained from MAPLE, red equations are the command lines and the blue equations are the solutions.

Equilibrium constants for Scheme 2 defined as:

$$K_1 = Zn \cdot OR / ZnOR,$$

$$K_d = ZnOR^2 \cdot OR^2 / ZnORD,$$

Material balance under assumption that  $OR \ll OR_t$  (under the experimental conditions where the  $\text{pH}$  is approximately 10 or less, the free  $OR \sim 10^{-7} \text{M}$  or less, and the total amount of added methoxide,  $OR_t \sim 10^{-3} \text{M}$ )

$$Zn_t = Zn + ZnOR + 2 \cdot ZnOR^2 \cdot OR^2 / K_d,$$

$$OR_t = ZnOR + 4 \cdot ZnOR^2 \cdot OR^2 / K_d$$



```
> solvefor[Zn] ( K1=Zn*OR/ZnOR, Kd=ZnOR^2*OR^2/ZnORD,
Znt=Zn+ZnOR+2*ZnOR^2*OR^2/Kd, ORt=ZnOR + 4*ZnOR^2*OR^2/Kd
);
```

$$\left\{ \begin{aligned} ZnORD &= \frac{ZnOR^2 OR^2}{Kd}, ORt = \frac{ZnOR (Kd + 4 ZnOR OR^2)}{Kd} \\ Zn &= - \frac{-Znt Kd + ZnOR Kd + 2 ZnOR^2 OR^2}{Kd} \\ K1 &= - \frac{(-Znt Kd + ZnOR Kd + 2 ZnOR^2 OR^2) OR}{Kd ZnOR} \end{aligned} \right\}$$

We solve the second and forth above equations for OR:

```
> solvefor[OR] (ORt = ZnOR*(Kd+4*ZnOR*OR^2)/Kd, K1 = - (-
Znt*Kd+ZnOR*Kd+2*ZnOR^2*OR^2)*OR/(Kd*ZnOR) );
>
```

$$\left[ \begin{aligned} &\left\{ \begin{aligned} OR &= \frac{\sqrt{ORt Kd - ZnOR Kd}}{2 ZnOR} \\ K1 &= - \frac{\sqrt{ORt Kd - ZnOR Kd} (-2 Znt + ZnOR + ORt)}{4 ZnOR^2} \end{aligned} \right\}, \\ &\left\{ \begin{aligned} OR &= - \frac{\sqrt{ORt Kd - ZnOR Kd}}{2 ZnOR} \end{aligned} \right\} \end{aligned} \right]$$

$$K_I = \frac{\sqrt{OR_t K_d - ZnOR K_d} (-2 Z_{nt} + ZnOR + OR_t)}{4 ZnOR^2} \Bigg]$$

Then we solve the above  $K_I$  expression for  $Z_{nt}$ :

```
> solvefor[Znt] (K_I = -1/4*(OR_t*K_d-ZnOR*K_d)^(1/2)*(-2*Znt+ZnOR+OR_t)/ZnOR^2);
```

$$Z_{nt} = \frac{1}{2 \sqrt{OR_t K_d - ZnOR K_d}} (4 K_I ZnOR^2 + \sqrt{OR_t K_d - ZnOR K_d} ZnOR + \sqrt{OR_t K_d - ZnOR K_d} OR_t)$$

From the appearance of Figure 1 in the main paper, we see that there is a plateau region where added methoxide does not change the rate of reaction. For this region we assume that  $[ZnOR] \ll [OR_t]$ , so that one can simplify the above expression to the quadratic equation: (it will be shown later that this equation satisfactorily reproduces the experimental kinetic results at all concentrations of added OR).

$$ZnOR^2 * (2 * K_I / \sqrt{K_d * OR_t}) + ZnOR / 2 + OR_t / 2 - Z_{nt} = 0,$$

Which we solve for  $ZnOR$ :

```
> solvefor[ZnOR] (ZnOR^2*(2*K_I/sqrt(K_d*OR_t))+ZnOR/2 + OR_t/2-Znt=0);
```

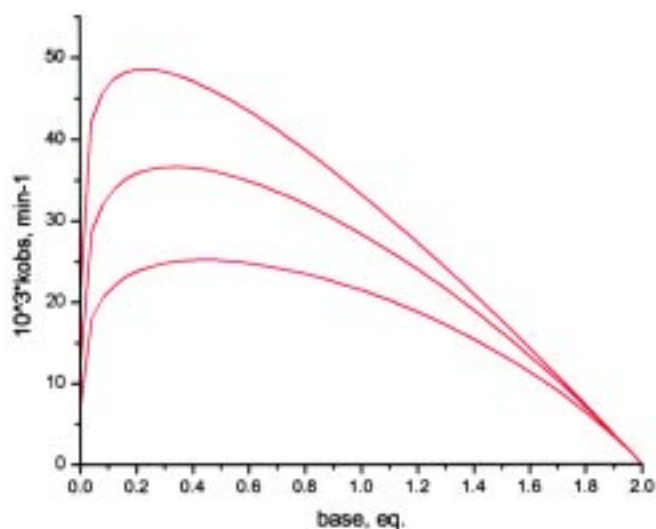
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$$\begin{aligned} ZnOR = & \frac{1}{8 K_I} (-\sqrt{OR_t K_d} \\ & + \sqrt{OR_t K_d - 16 K_I OR_t \sqrt{OR_t K_d} + 32 K_I Z_{nt} \sqrt{OR_t K_d}}), \\ ZnOR = & \frac{1}{8 K_I} (-\sqrt{OR_t K_d} \\ & - \sqrt{OR_t K_d - 16 K_I OR_t \sqrt{OR_t K_d} + 32 K_I Z_{nt} \sqrt{OR_t K_d}}) \end{aligned} \Bigg]$$

Rewriting the first real solution of the quadratic for clarity:

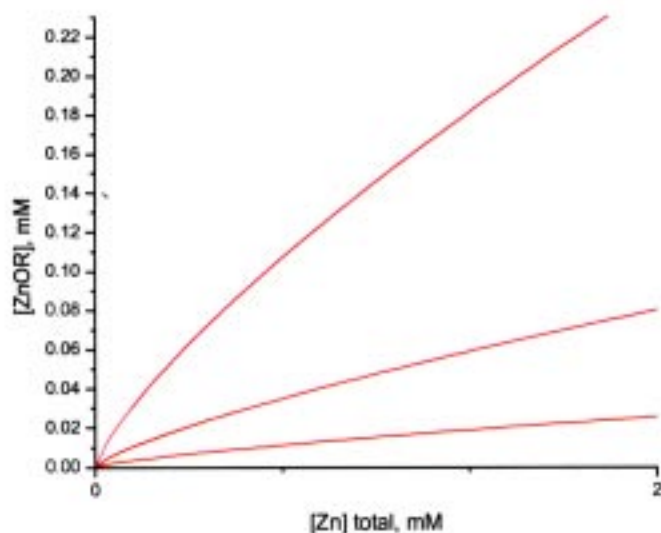
$$ZnOR = 1/8 * (-\sqrt{x * Kd} + \sqrt{x * Kd - 16 * K1 * x * \sqrt{x * Kd} + 32 * K1 * Znt * \sqrt{x * Kd}}) / K1$$

Shown in Figures 9S to 11S are the predicted rate constant curves based on the above equation derived for Scheme 2 using the indicated parameters.



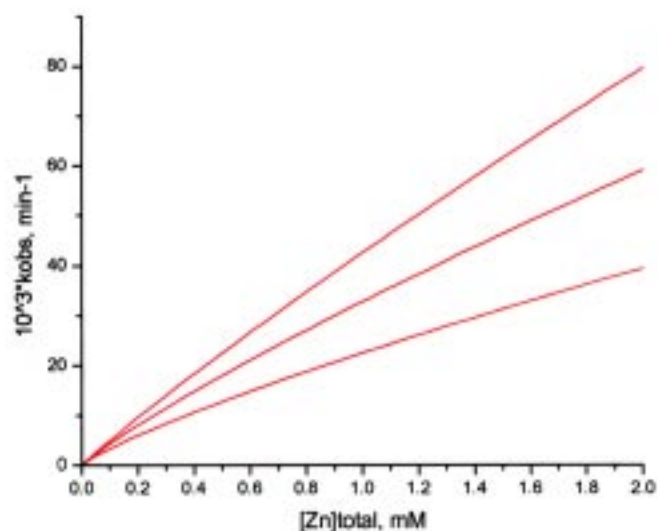
**Figure 9S, Computed plots of  $k_{obs}$  vs. added  $[OCH_3]$  generated using the following parameters:**

$K1 = 10^{-4} \text{ mM}$ ;  
 $Kd = 10^{-5}; 10^{-6}; 10^{-7} \text{ mM}$   
 $[Zn]_{total} = 1 \text{ mM}$   
 $k_{cat} = 34 \text{ M}^{-1} \text{ min}^{-1}$



**Figure 10S, Computed plots of dependence of the [ZnOR] vs. varying [Zn]<sub>t</sub>, under conditions where the [OR]<sub>t</sub> / [Zn]<sub>t</sub> is held constant at 0.3 generated using the following parameters:**

$K_1 = 10^{-4} \text{ mM}$ ;  
 $K_d = 10^{-10}, 10^{-12}, 10^{-14} \text{ mM}$   
 $[\text{OR}]_t / [\text{Zn}]_t = 0.3$



**Figure 11S, Computed plots of  $k_{\text{obs}}$  vs. added [Zn]<sub>t</sub>, under conditions where the [OR]<sub>t</sub> / [Zn]<sub>t</sub> is held constant at 0.3 generated using the following parameters:**

$K_1 = 10^{-4} \text{ mM}$ ;  
 $K_d = 10^{-5}, 10^{-6}, 10^{-7} \text{ mM}$   
 $[\text{OR}]_t / [\text{Zn}]_t = 0.3$

$$k_{\text{cat}} = 34 \text{ M}^{-1} \text{ min}^{-1}$$

Above we have derived an equation based on Scheme 2 for the  $[\text{Zn}^{2+}(\text{OCH}_3)]$  under some assumptions. It is clear that the predicted curves for the dependencies of the observed rate constants for the reactions correlate well with what is observed in Figures 1 and 2 of the main manuscript. In particular, we have verified that a dimer model satisfactorily reproduces the behaviour of Figure 1, maximizing at a  $[\text{OCH}_3]_{\text{t}} / [\text{Zn}]_{\text{t}}$  of 0.2-0.4. In addition, at a fixed  $[\text{OCH}_3]_{\text{t}} / [\text{Zn}]_{\text{t}}$  ratio of 0.3, the dimer model satisfactorily reproduces the appearance of Figure 2. We conclude that the simplified speciation shown in Figure 2 is sufficient to explain the experimental results.