Supplementary Material (ESI) for New Journal of Chemistry

Reaction Kinetics and mechanisms of neonicotinoid pesticides with sulphate radicals

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Supporting Information:

S.I. 1- Kinetic treatment of time-resolved sulphate radicals absorbance profiles.

From time-resolved experiments we monitor the decay rate of $SO_4^{\cdot-}$ radicals, and determine a pseudo first order rate constant obtained from these decays (k_{app}). In the absence of insecticides, sulphate radicals decay because of their reactions with $Na_2S_2O_8$ and HO^- anions. Since these experimental conditions remain constant throughout the set of experiments we will call the apparent rate constant measured in the absence of insecticides k_0. $SO_4^{\cdot-}$ radicals recombination is of no significance under our experimental conditions of high $[Na_2S_2O_8]$, since otherwise, a mixed first and second order decay would have been observed. In experiments with increasing Insecticide concentrations, k_{app} values become higher due to the reaction of $SO_4^{\cdot-}$ radicals and the insecticides. The measured k_{app} is now due to all these reactions competing for $SO_4^{\cdot-}$. Solution of the mass balance differential equations for $SO_4^{\cdot-}$ radicals yields $k_{app} = k_0 + k_2 \times [Ins]$. Therefore, the slope of the linear plots of k_{app} vs. [Ins] yield the value of k_2.

Table 1. Mulliken atomic charges of C1 and C2 atoms in the radical cation **rc** for the three insecticides. See Scheme 2 in the main text for the position of the carbon atoms.

	C1	C2
ACT	-0.35	-1.47
THIA	-0.32	-1.23

IMD	-0.24	-1.10

Figure 1. TD-DFT calculated spectra for the α-aminoalkyl radicals ACTRX (grey line) and ACTRY (black line). The dashed lines stand for the TD-DFT calculated spectra for the same radicals protonated in the pyridine ring.