Experimental and theoretical approaches on the reaction mechanism and kinetics of dimethyl 2-(6-oxopyridazin-1(6H)-yl)fumarate: micelle and salt effects

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**Supplemental Materials**

Rate law derivation in the absence of SDS according to the proposed mechanism (**Figure S ­­­­­­­8**):

*Step4 is RDS and steps 1 and 3 are in equilibrium state*

Rate = k4[I3]

$\frac{d[I\_{3}]}{dt}=0$ steady state approximation

$$\frac{d[I\_{3}]}{dt}=k\_{3}\left[I\_{2}\right]\left[N\right]- k\_{-3}\left[I\_{3}\right]-k\_{4}\left[I\_{3}\right]=0\rightarrow \left[I\_{3}\right]=\frac{k\_{3}\left[I\_{2}\right][N]}{k\_{4}+k\_{-3}}$$

$$\frac{d\left[I\_{2}\right]}{dt}= k\_{-3}\left[I\_{3}\right]+k\_{2}\left[I\_{1}\right]\left[2\right]-k\_{3}\left[I\_{2}\right]\left[N\right]=0$$

$k\_{-3}\left[I\_{3}\right]$ can be neglected, So $\left[I\_{2}\right]=\frac{k\_{2}\left[I\_{1}\right][2]}{K\_{3}[N]}$

$$\frac{d[I\_{1}]}{dt}=k\_{1}\left[1\right]\left[3\right]- k\_{-1}\left[I\_{1}\right]-k\_{2}\left[I\_{1}\right][2]=0\rightarrow \left[I\_{1}\right]=\frac{k\_{1}\left[1\right][3]}{k\_{-1}+k\_{2}[2]}$$

So, the following expression can be written

$$(Rate)\_{mech}=\frac{k\_{1}k\_{2}k\_{4}\left[1\right]\left[2\right][3]}{(k\_{-3}+k\_{4})(k\_{-1}+k\_{2}\left[2\right])}$$

Because the first step is fast then k-1>>k2 [2] and according to assumption of k4 as RDS, step k-3 >> k4 so the (rate)mech law can be introduced as the following expression:

$(Rate)\_{mech}=\frac{k\_{1}k\_{2}k\_{4}\left[1\right]\left[2\right][3]}{k\_{-3}k\_{-1}}$

And we have:

$$k\_{obs}=\frac{k\_{1}k\_{2}k\_{4}\left[3\right]}{k\_{-3}k\_{-1}}$$

So:

$$(Rate)\_{mech}=k\_{obs}\left[1\right][2]$$

Rate law derivation in the presence of SDS (**Figure S 14**):

*Step5 is RDS and steps 1 and 4 are in equilibrium state*

Rate = k5[I4]

$\frac{d[I\_{4}]}{dt}=0$ steady state approximation

$$\frac{d[I\_{4}]}{dt}=k\_{4}\left[I\_{3}\right]\left[N\right]- k\_{-4}\left[I\_{4}\right][SDS]-k\_{5}\left[I\_{4}\right]=0\rightarrow \left[I\_{4}\right]=\frac{k\_{4}\left[I\_{3}\right][N]}{k\_{5}+k\_{-4}[SDS]}$$

$$\frac{d\left[I\_{3}\right]}{dt}= k\_{3}\left[I\_{2}\right][SDS]+k\_{-4}\left[I\_{4}\right]\left[SDS\right]-k\_{4}\left[I\_{3}\right]\left[N\right]=0$$

$k\_{-4}\left[I\_{4}\right][SDS]$ can be neglected, So $\left[I\_{3}\right]=\frac{k\_{3}\left[I\_{2}\right][SDS]}{k\_{4}[N]}$

$$\frac{d[I\_{2}]}{dt}=k\_{2}\left[I\_{1}\right][N]- k\_{3}\left[I\_{2}\right][SDS]=0\rightarrow \left[I\_{2}\right]=\frac{k\_{2}\left[I\_{1}\right][N]}{k\_{3}[SDS]}$$

$$\frac{d[I\_{1}]}{dt}=k\_{1}\left[1\right]\left[3\right]- k\_{-1}\left[I\_{1}\right]-k\_{2}\left[I\_{1}\right][2]=0\rightarrow \left[I\_{1}\right]=\frac{k\_{1}\left[1\right][3]}{k\_{-1}+k\_{2}[2]}$$

So, the following expression can be written

$$(Rate)\_{mech}=\frac{k\_{1}k\_{2}k\_{5}\left[1\right]\left[2\right][3]}{(k\_{-4}[SDS]+k\_{5})(k\_{-1}+k\_{2}\left[2\right])}$$

Because the first step is fast then k-1>>k2[2] and according to assumption of RDS for step5, k-4 >> k5  so:

 $\left(Rate\right)\_{mech}=\frac{k\_{1}k\_{2}k\_{5}\left[1\right]\left[2\right]\left[3\right]}{k\_{-4}\left[SDS\right]k\_{-1}}$

and

$k\_{obs}=\frac{k\_{1}k\_{2}k\_{5}[3]}{k\_{-4}[SDS]k\_{-1}}$

So we have:

(Rate)mech = kobs[1][2]

***Pseudo order condition for partial orders determination***



**Figure S 1.** First order fit on the reaction among **(1), (2)** and **(3)** when **(2)** is in excess and **(3)** is catalyst.



**Figure S 2.** First order fit on the reaction among **(1), (2)** and **(3)** when **(1)** is in excess and **(3)** is catalyst

***Change in absorbance during the time in ethanol solvent***



**Figure S 3.** Second order fitting curve (solid line) for product absorbance versus time at 360 nm wavelength in ethanol at 28°C in the reaction between 10-2 M of **(1)**, 10-2 M of **(2)** in the presence of 5×10-3 M of **(3).**

The effect of temperature and activation parameters determination

**Figure S 4.** Dependence of ln k on reciprocal temperature for the reaction among **(1), (2)** and **(3)** in order to evaluate Ea/R from the slope according to the Arrhenius equation

**Figure S 5.** Dependence of ln k/T on reciprocal temperature for the reaction among **(1), (2)** and **(3)** in order to evaluate activation parameters (ΔH‡ and ΔS‡, respectively) from the slope and intercept according to the Eyring equation (8)

**Figure S 6.** Dependence of Tlnk/T on reciprocal temperature for the reaction among **(1), (2)** and **(3)** in order to evaluate activation parameters (ΔS‡ and ΔH‡, respectively) from the slope and intercept, according to the linearized form of the Eyring equation (9).

**Salt effect on the reaction rate**



**Figure S 7.** Rate constant dependence on ionic strength (*I*) of NaBr for the reaction among reactants **(1), (2)** and **(3)** in methanol solvent at 28°C



**Figure S 8**. Simplified form of the speculative mechanism for the reaction among **(1), (2)** and **(3)** in the absence of SDS.

**The effect of SDS on the reaction**



**Figure S 9.** No reaction between DMAD (1) and SDS (micelle)

 

**Figure S 10.** No reaction between 3-(2H) pyridazinone (2) and SDS (micelle)



**Figure S 11.** No reaction between AsPh3 (3) and SDS (micelle)



**Figure S 12.** The reaction between DMAD **(1)** and AsPh3 **(3)** in the presence of SDS, spectrum (b1) and in the absence of SDS, spectrum (a1).



**Figure S 13.** Speculative mechanism for the reaction among **(1), (2)** and **(3)** in the presence of SDS.



**Figure S 14.** Simplified form of the speculative mechanism of the reaction among **(1), (2)** and **(3)** in the presence of SDS.

**Computational study**



**Figure S 15.** T.S structure (T.S4) in step4 optimized by DFT method at the B3LYP/6-31+G(2d,p) level of theory in gas phase

**Table S 1.** Volume quantities (μL) of reactants **(1), (2)** and **(3)** that have been used to satisfy Job’s plot.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| reactants |  |  | Volume (μL) |  |  |  |
| **(1)** | 1000 | 800 | 600 | 400 | 200 | 0 |
| **(2)** | 0 | 100 | 200 | 300 | 400 | 500 |
| **(3)** | 0 | 100 | 200 | 300 | 400 | 500 |

**Table S 2.** Comparison between the experimental rate law (Rate)exp and the derived rate law (Rate)mech law when each step (step1 , step2 , step3,  step4,  step5) has been considered as RDS.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| RDS step  | Equilibrium step(s)  | (Rate)mech  | kobs  | ( Rate)exp  |
| 1  | 1  | kobs[1]  | k1[3]  | kobs[1][2]  |
| 2  | 1  | kobs[1][2]  | $$\frac{k\_{1}k\_{2}[3]}{k\_{-1}}$$ | kobs[1][2]  |
| 3  | 1&2  | $$\frac{k\_{1}k\_{2}k\_{3}\left[1\right]\left[2\right][3]}{(k\_{-2})(k\_{-1}+k\_{2}\left[2\right])}$$ |    | kobs[1][2]  |
| 4 | 1&3  | kobs[1][2] | $$\frac{k\_{1}k\_{2}k\_{4}[3]}{(k\_{-3})(k\_{-1})}$$ | kobs[1][2] |
| 5  | 1&4  | kobs[1][2]  | $$\frac{k\_{1}k\_{2}k\_{5}[3]}{(k\_{-4})(k\_{-1})}$$ | kobs[1][2]  |

**Table S 3.** The first stretching frequencies (cm-1) for the steps 2 and 4 of the reaction mechanism calculated by DFT method at B3LYP/6-31+G(2d,p) level of theory in gas phase

|  |  |  |  |
| --- | --- | --- | --- |
| Step2 | first stretching frequency (cm-1) | Step 4 | first stretching frequency (cm-1) |
| I1 | 9.25 | I3 | 17.55 |
| T.S2 | -906.61 | T.S4 | -1548.63 |
| I2 | 17.67 | P | 6.66 |