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Supplementary Materials

J4816-1

Mechanism in Polyoxometalate-Catalyzed Homogeneous Hydrocarbon Oxo Transfer Oxidation. The $[\text{Co}_4(\text{H}_2\text{O})_2\text{P}_2\text{W}_{18}\text{O}_{68}]^{10-}$ / *p*-cyano-*N,N*-dimethylaniline *N*-Oxide Selective Catalytic Epoxidation System.

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Figure S1. An Example of the Initial Rate Determination. Reaction conditions: 0.0566M CDMANO, 0.0022M **1**, 1.97 M cyclohexene, argon atmosphere, 50 °C, 700 rpm stir rate, and acetonitrile solvent. Aliquots quenched by 1:1 v/v CS_2 : CH_2Cl_2 before GC analysis.

Figure S2. Stack Plot of Absorbance Change vs. Time. Conditions: 0.004 M **1**, 0.04 M CDMANO, 25 °C under Ar, 650 rpm stir rate, and acetonitrile solvent. Spectra from 450 to 700 nm taken at 15 s, 36 s, 60 s, 2.5 min, 5 min, 7 min, 10 min, 15 min, 25.5 min, 40 min, 60 min, 95 min, 126 min, 180 min and 240 min after addition of CDMANO.

Figure S3. Difference Spectra of Figure S2. UV-visible spectrum at time *t* minus spectrum at *t* = 15 s.

Figure S4. Experimentally Determined Rate Law.

Figure S5. Effect of CDMA on the Rate of Epoxidation. Conditions: 0.0566 M CDMANO, 0.0022 M **1**, 1.20 M cyclohexene, and 0%, 8%, 22%, and 40% weight percent CDMA relative to total CDMANO added for different data points in the plot, 50 °C under Ar, 700 rpm stir rate, and acetonitrile solvent.

Figure S6. Derivation of the Theoretical Rate Law for Scheme 3.

Figure S7. Raw Kinetics Data. Epoxidation rate dependence on concentration of cyclohexene, CDMANO and catalyst.

J4816-2

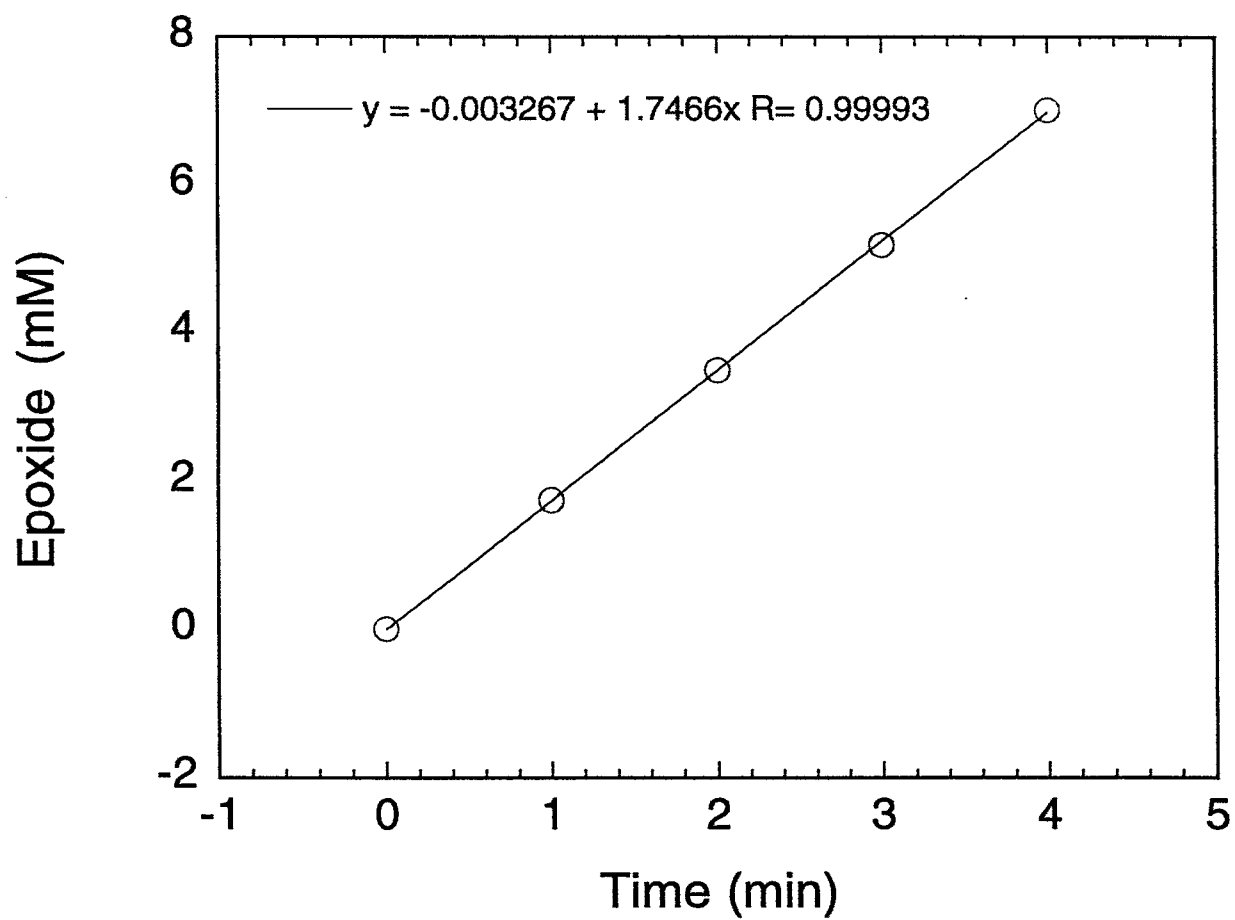


Figure S1

J4816-3

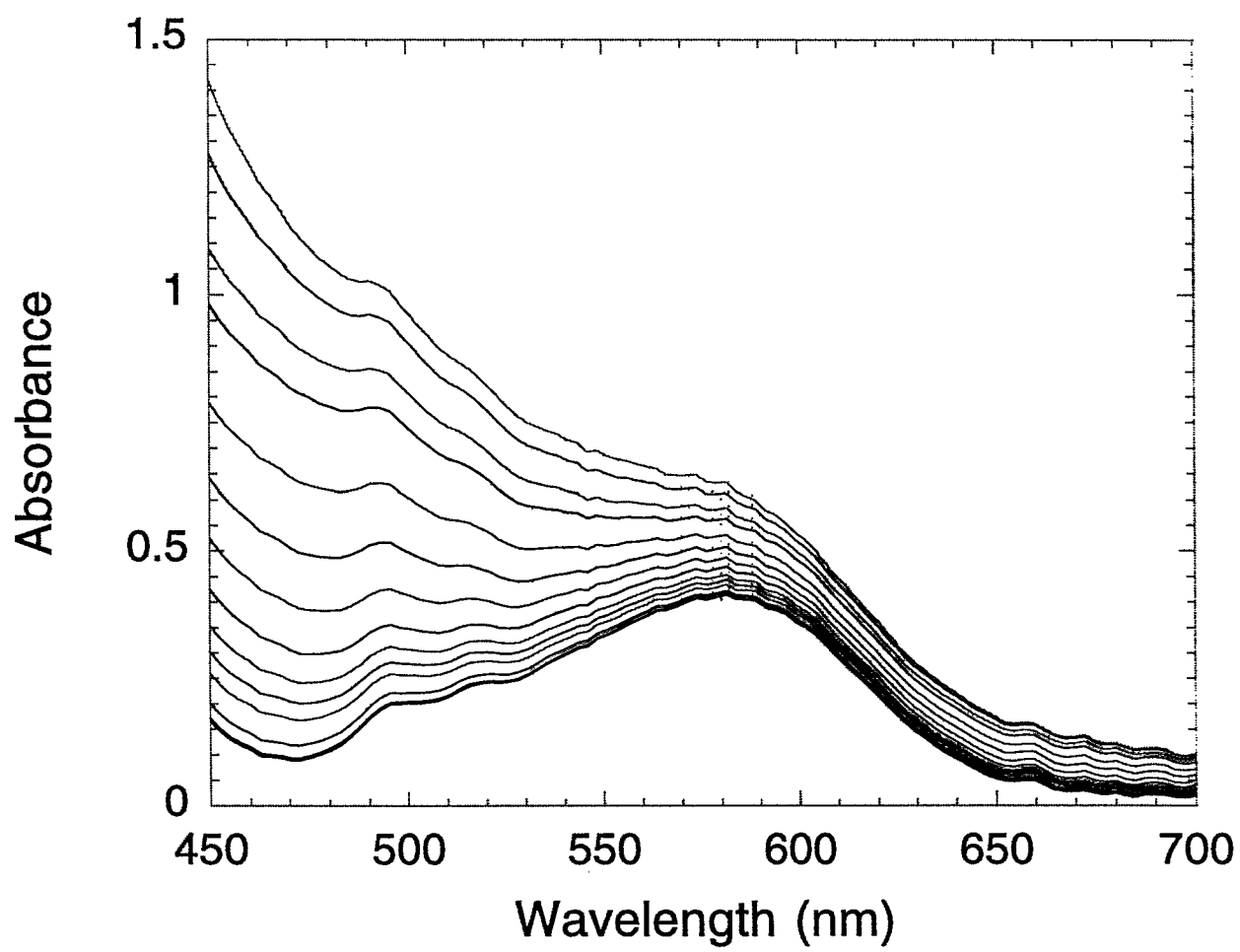


Figure S2

J4816-4

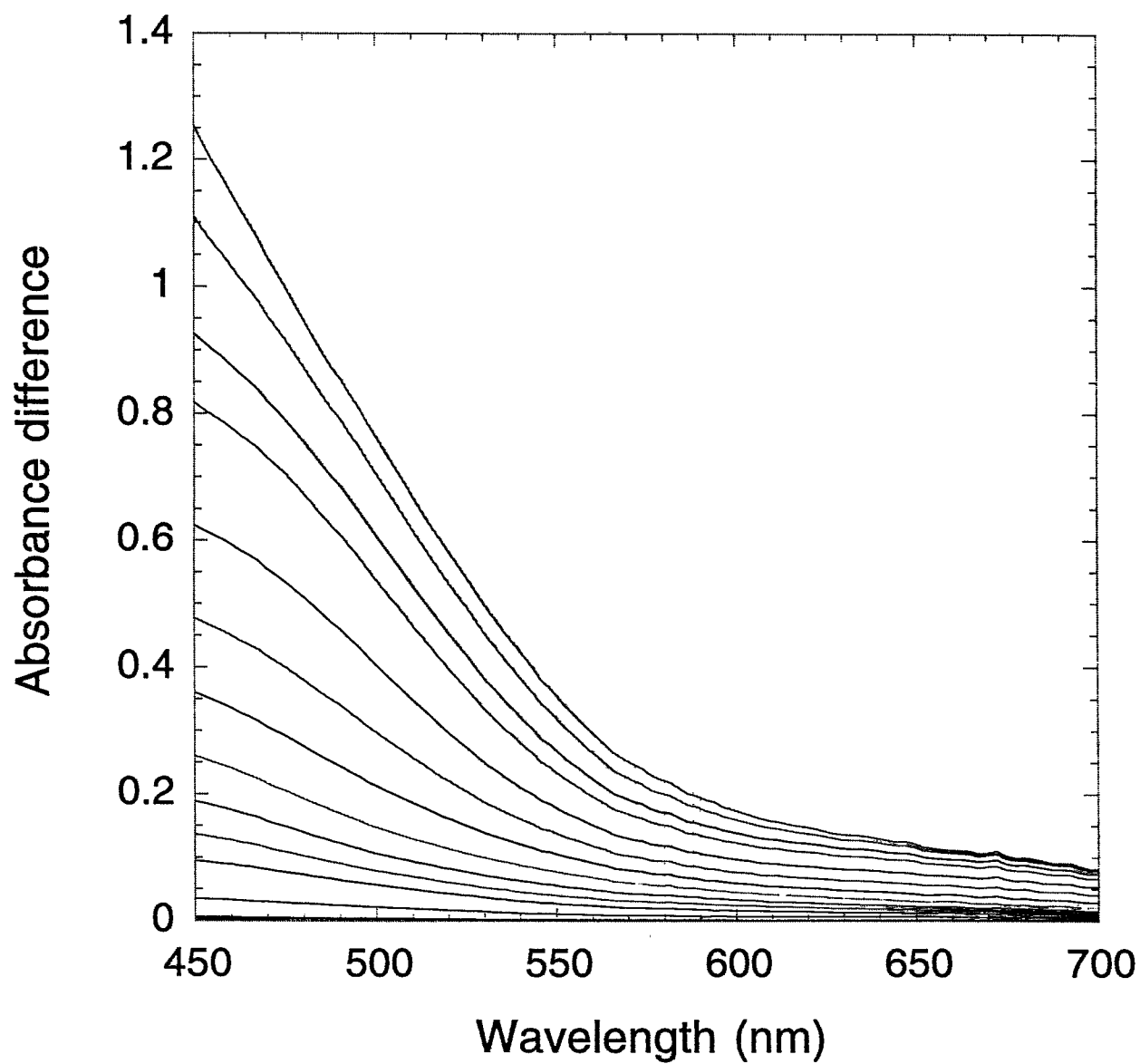


Figure S3

From the epoxidation rate dependence on the concentration of catalyst, we have:

$$\text{rate} = a [1]_{\text{tot}} \quad (1)$$

Since the initial concentration of cyclohexene and CDMANO are constants, terms related to cyclohexene and CDMANO are included in the term a .

From the epoxidation rate dependence on the concentration of CDMANO, we have:

$$\begin{aligned} 1 / \text{rate} &= 1 / b [\text{CDMANO}] + c \\ \text{rate} &= \frac{b [\text{CDMANO}]}{c b [\text{CDMANO}] + 1} \end{aligned} \quad (2)$$

Since initial concentration of cyclohexene is constant, terms related to cyclohexene and catalyst are included in the terms b and c .

From the epoxidation rate dependence on the concentration of cyclohexene, we have:

$$\begin{aligned} 1 / \text{rate} &= 1 / d [\text{cyclohexene}] + e \\ \text{rate} &= \frac{d [\text{cyclohexene}]}{d e [\text{cyclohexene}] + 1} \end{aligned} \quad (3)$$

Again, the terms related to CDMANO and catalyst are included in the terms d and e .

Combining eqs 1, 2, and 3 gives the $[\text{CDMANO}]$, $[\text{cyclohexene}]$, and $[1]_{\text{tot}}$ term in the numerator. In the denominator, we should have a constant times $[\text{CDMANO}]$ term, a constant times $[\text{cyclohexene}]$ term, and a constant term. However, since we are using the initial rate method, in eq 2 a $[\text{cyclohexene}]$ term might be buried within the constant term, b or c . Also, in eq 3 a $[\text{CDMANO}]$ term might be buried within the constant term d or e . Therefore, the constant term in the denominator can contain two terms: one is a plain constant and the other is a constant times $[\text{CDMANO}] [\text{cyclohexene}]$. Overall we have:

$$\text{rate} = \frac{k' [\text{cyclohexene}] [\text{CDMANO}] [1]_{\text{tot}}}{k'' [\text{CDMANO}] + k''' [\text{cyclohexene}] + k'''' [\text{CDMANO}] [\text{cyclohexene}] + k''''}$$

J4816-6

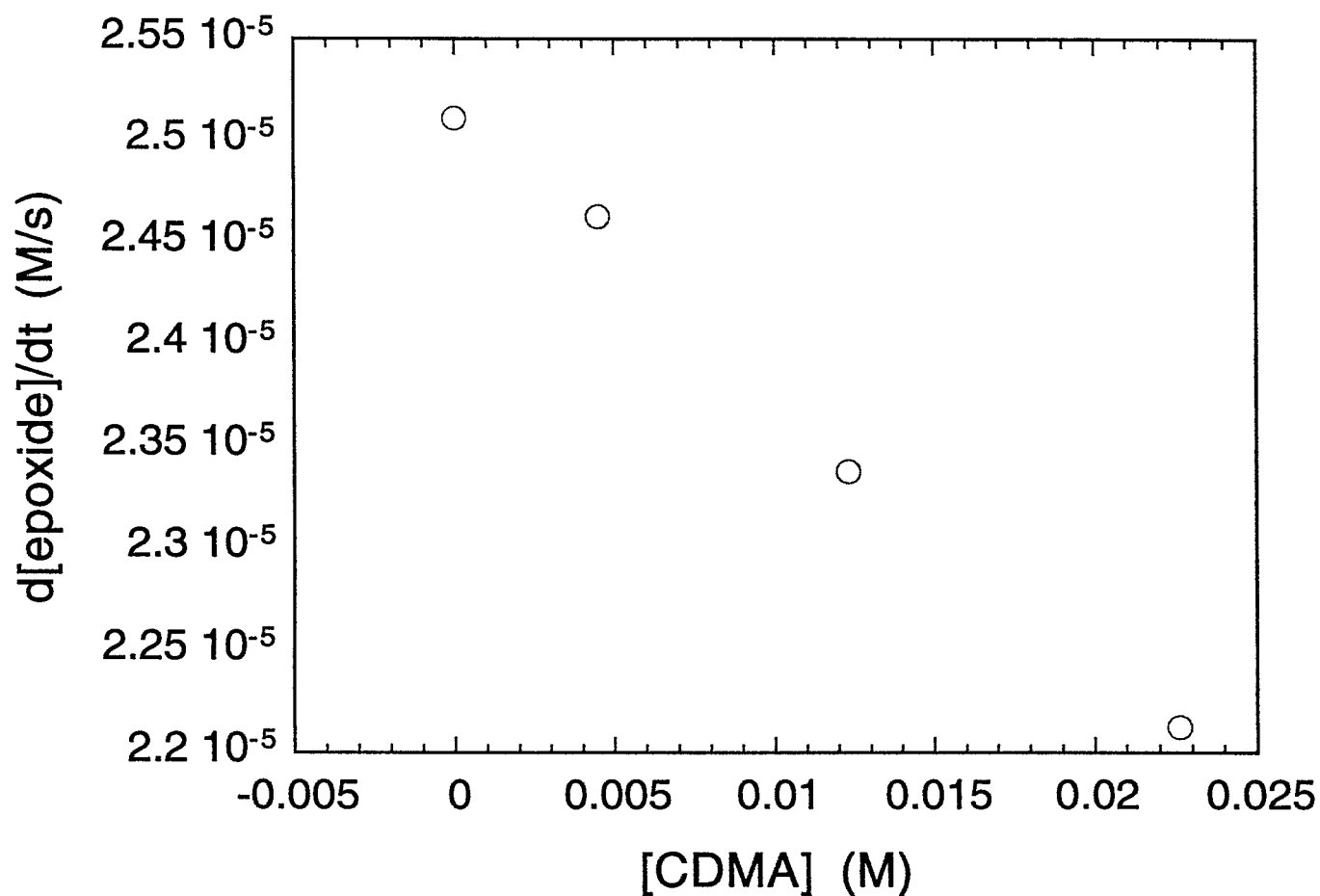
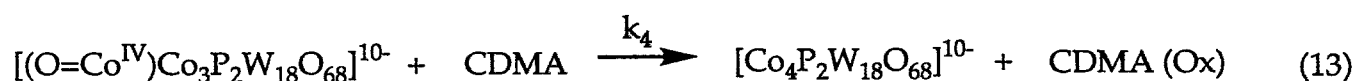
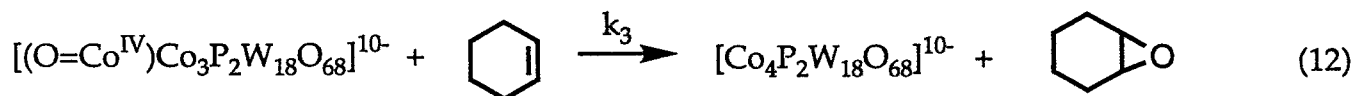
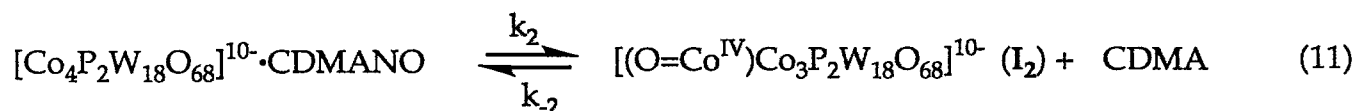
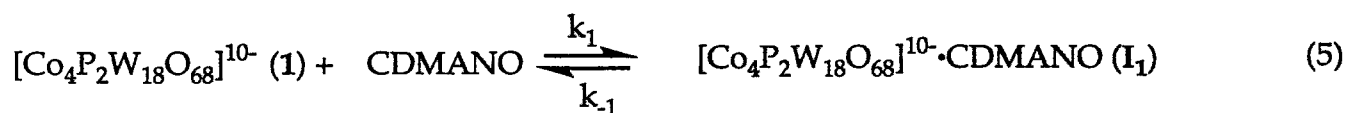


Figure S5

J4816-7



$$\text{rate} = d[\text{epoxide}]/dt = k_3 [\text{I}_2] [\text{cy}] \quad (14)$$

From eq 5:

$$[\text{I}_1] = K_1 [1] [\text{ox}] \quad (15)$$

Using steady state approximation

$$d[\text{I}_2]/dt = k_2 [\text{I}_1] - k_{-2} [\text{I}_2] [\text{an}] - k_3 [\text{I}_2] [\text{cy}] - k_4 [\text{I}_2] [\text{an}] = 0 \quad (16)$$

Since the catalyst is distributed in 3 forms:

$$[1]_{\text{tot}} = [1] + [\text{I}_1] + [\text{I}_2] \quad (17)$$

Substitute eq 15 into eq 17, we have:

$$[1]_{\text{tot}} = [\text{I}_1] + [\text{I}_2] + \frac{[\text{I}_1]}{K_1 [\text{ox}]}$$

$$[\text{I}_1] = \frac{K_1 [\text{ox}] ([1]_{\text{tot}} - [\text{I}_2])}{1 + K_1 [\text{ox}]} \quad (18)$$

Substitute eq 18 into eq 16

$$\frac{k_2 K_1 [\text{ox}] ([1]_{\text{tot}} - [\text{I}_2])}{1 + K_1 [\text{ox}]} - (k_{-2} + k_4) [\text{I}_2] [\text{an}] - k_3 [\text{I}_2] [\text{cy}] = 0 \quad (19)$$

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Continue with eq 19

$$k_2 K_1 [\text{ox}] [\mathbf{1}]_{\text{tot}} - k_2 K_1 [\text{ox}] [\text{I}_2] - k_3 K_1 [\text{I}_2] [\text{cy}] [\text{ox}] - (k_{-2} + k_4) K_1 [\text{I}_2] [\text{an}] [\text{ox}] - k_3 [\text{I}_2] [\text{cy}] - (k_{-2} + k_4) [\text{I}_2] [\text{an}] = 0 \quad (20)$$

$$k_2 K_1 [\text{ox}] [\text{I}_2] + (k_{-2} + k_4) K_1 [\text{I}_2] [\text{an}] [\text{ox}] + k_3 K_1 [\text{I}_2] [\text{cy}] [\text{ox}] + k_3 [\text{I}_2] [\text{cy}] + (k_{-2} + k_4) [\text{I}_2] [\text{an}] = k_2 K_1 [\text{ox}] [\mathbf{1}]_{\text{tot}} \quad (21)$$

$$[\text{I}_2] = \frac{k_2 K_1 [\text{CDMANO}] [\mathbf{1}]_{\text{tot}}}{k_2 K_1 [\text{ox}] + (k_{-2} + k_4) K_1 [\text{an}] [\text{ox}] + k_3 K_1 [\text{cy}] [\text{ox}] + k_3 [\text{cy}] + (k_{-2} + k_4) [\text{an}]} \quad (22)$$

Substitute eq 22 into eq 14

$$\text{rate} = \frac{k_2 k_3 K_1 [\text{CDMANO}] [\text{cy}] [\mathbf{1}]_{\text{tot}}}{k_2 K_1 [\text{ox}] + (k_{-2} + k_4) K_1 [\text{an}] [\text{ox}] + k_3 K_1 [\text{cy}] [\text{ox}] + k_3 [\text{cy}] + (k_{-2} + k_4) [\text{an}]} \quad (23)$$

J4816-9

Table I. Epoxidation rate vs. concentration of cyclohexene.

Concentration (M)	Rate (M/s)
0.12	4.7×10^{-6}
0.25	8.7×10^{-6}
0.39	1.2×10^{-5}
0.59	1.5×10^{-5}
0.79	1.8×10^{-5}
1.1	2.2×10^{-5}
1.4	2.5×10^{-5}
1.6	2.6×10^{-5}
2.0	2.9×10^{-5}

Table II. Epoxidation rate vs. concentration of CDMANO.

Concentration (M)	Rate (M/s)
0.011	8.7×10^{-6}
0.027	1.5×10^{-5}
0.057	2.2×10^{-5}
0.092	2.7×10^{-5}
0.13	3.0×10^{-5}
0.17	3.2×10^{-5}

Table III. Epoxidation rate vs. concentration of catalyst.

Concentration (mM)	Rate (M/s)
0.62	6.5×10^{-6}
1.0	1.0×10^{-5}
1.7	1.6×10^{-5}
2.2	2.2×10^{-5}
3.0	2.9×10^{-5}
3.9	3.7×10^{-5}

Figure S7.