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SUPPORTING INFORMATION

ADDITION / CORRECTION FOR:

Hornstein, B. J.; Finke, R. G. *Chem. Mater*, **2004**, *16*, 139-150.

Transition-Metal Nanocluster Kinetic and Mechanistic Studies Emphasizing Nanocluster Agglomeration: Demonstration of a Kinetic Method that Allows Monitoring of All Three Phases of Nanocluster Formation and Aging

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Appendix A: Treatment of the Kinetic Data

The following is a corrected version of the Supporting Information accompanying the original paper;[1] it replaces that Supporting Information except for the section entitled "The Experimental Methods to Determine y", Figures S1, S2 and S3.[1]

The revised equations are (3a)-(3e) and (4) below, six total equations which replace the five prior equations (3a)-(3d) and (4) in the main text elsewhere:[1]

$$\alpha x \left[\; A \underset{H_2}{\overset{k_1}{\rightarrow}} B \; \right] \tag{3a}$$

$$\alpha(1\text{-}x) \left[\; A + B \underset{H_2}{\overset{k_2}{\rightarrow}} 2\,B \; \right] \tag{3b}$$

$$1400 \left[\; B + \text{cyclohex}\textit{ene} + H_2 \overset{\text{fast}}{\rightarrow} B + \text{cyclohex}\textit{ane} \; \right] \tag{3c}$$

$$\underline{\text{SUM:}} \quad \alpha A + 1400\ \text{cyclohex}\textit{ene} + 1400\ H_2 \overset{k_{SUM}}{\rightarrow} \alpha B + 1400\ \text{cyclohex}\textit{ane} \tag{3d}$$

$$1/2 \left[\; B + B \overset{k_3}{\rightarrow} 2(1 - y)B + 2yC \; \right] \tag{3e}$$

$$(\text{or } yB \rightarrow yC)$$

$$\underline{\text{NET REACTION:}} \quad A \rightarrow (1-y)B + yC \tag{4}$$

The variable, α, is experimentally the amount of A converted (measured as the amount of cyclooctane released; determined by GLC) at the time the cyclohexene has been fully consumed

[1] Hornstein, B. J.; Finke, R. G. *Chem. Mater*, **2004**, *16*, 139-150.

(see equation (3d) above); that is, $\alpha \approx 0.7$ for the experiment in Figure 2 of the main text with 2 equivalents of pyridine[1] (i.e., at ~2.5 h when the cyclohexene concentration is zero, only about 0.7 eq. of cyclooctane has evolved corresponding to the consumption of 0.7 eq A; approximately 10 h is required for the full consumption of A, see Figure S4).

From equation (3d) we can see equation A.1

A.1 $$\left(\frac{1}{\alpha}\right)\frac{d[A]}{dt} = \left(\frac{1}{1400}\right)\frac{d[\text{cyclohexene}]}{dt}$$

Integrating from A = $[A]_o$ to $[A]_t$ and cyclohexene = $[\text{cyclohexene}]_o$ to $[\text{cyclohexene}]_t$ yields equation A.2.

A.2 $$\frac{1}{\alpha}\left([A]_t - [A]_o\right) = \frac{1}{1400}\left([\text{cyclohexene}]_t - [\text{cyclohxexene}]_o\right)$$

A.3(a) but for 1400 $A_o = \alpha[\text{cyclohexene}]_o$, it follows that

A.3(b) $$[\text{cyclohexene}]_t = \frac{1400}{\alpha}[A]_t$$

Differentiating equation A.3(b) with respect to time yields equation A.3 (c)

A.3(c) $$\frac{d[\text{cyclohexene}]}{dt} = \frac{1400}{\alpha}\frac{d[A]}{dt}$$

MacKinetics Numerical Integration Treatment of the Cyclohexene vs Time Data

The H_2 loss vs time for the cyclohexene hydrogenation, equation (3d), is followed vs time with a high precision pressure transducer. Those H_2 vs time data are then converted to [cyclohexene] loss vs time data via PV = nRT, the known volume of the system, and using the 1:1 H_2 to cyclohexene stoichiometry, equation (3d).

The kinetic equations entered into MacKinetics correspond to equations (3a), (3b) and (3e), namely equations A.4-A.6:

A.4 $$A \xrightarrow{k_1} B$$

A.5 $$A + B \xrightarrow{k_2} 2B$$

A.6 $$B + B \xrightarrow{k_3} C \quad \text{(where } C = B{\cdot}B\text{, i.e., } B_2\text{)}$$

$$\text{(i.e., } 2B \longrightarrow C\text{)}$$

The corresponding differential equations are A.7-A.9:

A.7 $$\frac{-d[A]}{dt} = k_1[A] + k_2[A][B]$$

A.8 $$\frac{d[B]}{dt} = k_1[A] + k_2[A][B] - 2k_3[B]^2$$

$$= \frac{-d[A]}{dt} - 2k_3[B]^2$$

A.9 $$\frac{d[C]}{dt} = k_3[B]^2$$

$$= -\frac{1}{2}\left(\frac{d[A]}{dt} + \frac{d[B]}{dt}\right)$$

The mass balance equation is A.10

A.10 $$[A]_o = [A]_t + [B]_t + 2[C]_t$$

(As a check $d[A]_o/dt = 0 = d[A]/dt + d[B]/dt + 2d[C]/dt$, and if one adds -A.7 + A.8 + 2A.9, that sum in fact = 0.)

However, for the ease of analysis of the data, we enter the $[\text{cyclohexene}]_o$ and $[\text{cyclohexene}]_t$ vs time data into MacKinetics. That is, the actual system numerically integrated is:

A.11 $\quad \text{cyclohexene} \xrightarrow{k_{1\,obs}} B'$

$\quad$ (i.e., $A' \xrightarrow{k_{1\,obs}} B'$ where A' = cyclohexene)

A.12 $\quad \text{cyclohexene} + B' \xrightarrow{k_{2\,obs}} 2B'$

$\quad$ (i.e., $A' + B' \xrightarrow{k_{2\,obs}} 2B'$)

A.13 $\quad B' + B' \xrightarrow{k_{3\,obs}} C'$

The differential equations corresponding to A.11-A.13 are:

A.14 $$\frac{-d[\text{cyclohexene}]}{dt} = \frac{-d[A']}{dt} = k_{1obs}[A'] + k_{2obs}[A'][B']$$

A.15 $$\frac{d[B']}{dt} = k_{1obs}[A'] + k_{2obs}[A'][B'] - 2k_{3obs}[B']^2$$

A.16 $$\frac{d[C']}{dt} = k_{3obs}[B']^2$$

The mass balance equation A.17 is easily derived by adding $\frac{d[A']}{dt} + \frac{d[B']}{dt} + 2\frac{d[C']}{dt}$, showing this equals zero, and then integrating (where $[B]_o = [C]_o = 0$).

A.17 $$[A']_o = [A']_t + [B']_t + 2[C']_t \text{ or } [A']_o - [A']_t = [B']_t + 2[C']_t$$

From equations A.3(a) and A.3(b) we are reminded that:

A.3(a) $$[\text{cyclohexene}]_o = [A']_o = \frac{1400}{\alpha}[A]_o$$

A.3(b) $$[\text{cyclohexene}]_t = [A']_t = \frac{1400}{\alpha}[A]_t$$

Combining these equations with A.17 yields:

A.18(a) $$[A']_o - [A']_t = \frac{1400}{\alpha}([A]_o - [A]_t) = [B']_t + 2[C']_t$$

But substituting equation A.10 yields

A.18(b) $$\frac{1400}{\alpha}([B]_t + 2[C]_t) = [B']_t + 2[C']_t$$

From which is follows that

A.18(c) $$\frac{1400}{\alpha}[B]_t + \left(\frac{1400}{\alpha}\right)2[C]_t = [B']_t + 2[C']_t$$

Which leads to the following identities:

A.18(d) $$\frac{1400}{\alpha}[B]_t = [B']_t$$

A.18(e) $$\frac{1400}{\alpha}[C]_t = [C']_t$$

Now we can substitute A.3(b), A.18(d) and A.18(e) into equations A.14, A.15 and A.16 to derive, ultimately, the desired relationship between k_{1obs}, k_{2obs}, k_{3obs} and k_1, k_2 and k_3.

A.19(a) $$\left(\frac{1400}{\alpha}\right)\frac{-d[A]}{dt} = \left(\frac{1400}{\alpha}\right)k_{1obs}[A] + \left(\frac{1400}{\alpha}\right)^2 k_{2obs}[A][B]$$

or A.19(b) $$\frac{-d[A]}{dt} = k_{1obs}[A] + \left(\frac{1400}{\alpha}\right)k_{2obs}[A][B]$$

A.20(a) $$\left(\frac{1400}{\alpha}\right)\frac{d[B]}{dt} = \left(\frac{1400}{\alpha}\right)k_{1obs}[A] + \left(\frac{1400}{\alpha}\right)^2 k_{2obs}[A][B] - \left(\frac{1400}{\alpha}\right)^2 2k_{3obs}[B]^2$$

or A.20(b) $$\frac{d[B]}{dt} = k_{1obs}[A] + \left(\frac{1400}{\alpha}\right)k_{2obs}[A][B] - \left(\frac{1400}{\alpha}\right)2k_{3obs}[B]^2$$

A.21(a) $$\left(\frac{1400}{\alpha}\right)\frac{d[C]}{dt} = \left(\frac{1400}{\alpha}\right)^2 k_{3obs}[B]^2$$

or A.21(b) $$\frac{d[C]}{dt} = \left(\frac{1400}{\alpha}\right)k_{3obs}[B]^2$$

Finally, a comparison of equations A.7, A.8 and A.9 with A.19(b), A.20(b) and A.21(b) yields the identities:

A.22 $$k_1 = k_{1obs}$$

A.23 $$k_2 = \left(\frac{1400}{\alpha}\right)k_{2obs}$$

A.24 $$k_3 = \left(\frac{1400}{\alpha}\right)k_{3obs}$$

Experimental Methods to Determine y

This section is unchanged from the prior Supporting Information. Note that for the net reaction, A → (1-y)B + yC (equation 4 herein), where y = y(t), the estimate of y = 0.45 determined on p. 146 elsewhere[1])for the case where 2 equivalents of pyridine were added) is just a single value of the variable y as detailed in the main text and the Experimental section elsewhere.[1]

Actual MacKinetics Treatment of the Raw Data Set Prior to Measuring y

This section can be completely discarded; it is replaced by, for example, equations A.22 – A.24 in this revised Supporting Information.

Figures S1, S2 and S3

Each of these Figures given in the prior Supporting Information is correct and remains unchanged.