

From Original Version 2.3
Correction Version 1_5 (4/7/04)

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

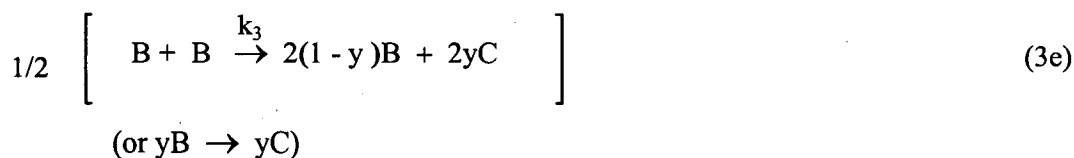
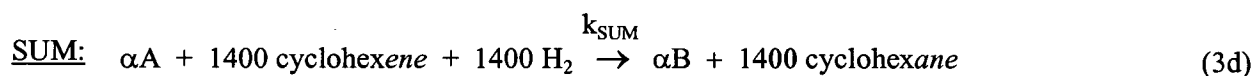
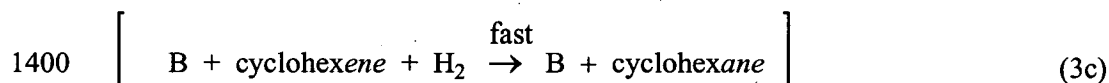
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Appendix A: Treatment of the Kinetic Data

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



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 pyridine¹ (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

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

Integrating from $A = [A]_0$ to $[A]_t$ and cyclohexene = $[\text{cyclohexene}]_0$ to $[\text{cyclohexene}]_t$ yields equation A.2.

$$\text{A.2} \quad \frac{1}{\alpha} ([A]_t - [A]_0) = \frac{1}{1400} ([\text{cyclohexene}]_t - [\text{cyclohexene}]_0)$$

A.3(a) but for $1400 A_0 = \alpha [\text{cyclohexene}]_0$, it follows that

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

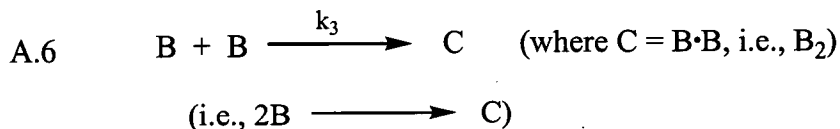
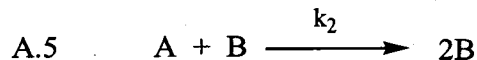
Differentiating equation A.3(b) with respect to time yields equation A.3 (c)

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

MacKinetics Numerical Integration Treatment of the Cyclohexene vs Time Data

The H₂ loss vs time for the cyclohexene hydrogenation, equation (3d), is followed vs time with a high precision pressure transducer. Those H₂ 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 H₂ to cyclohexene stoichiometry, equation (3d).

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



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

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

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

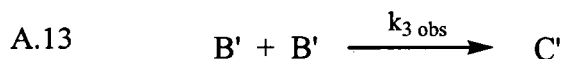
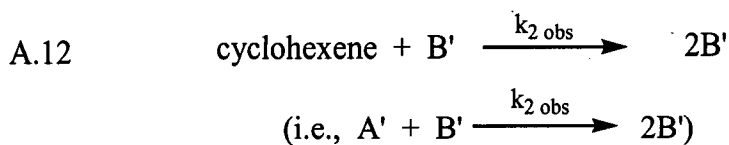
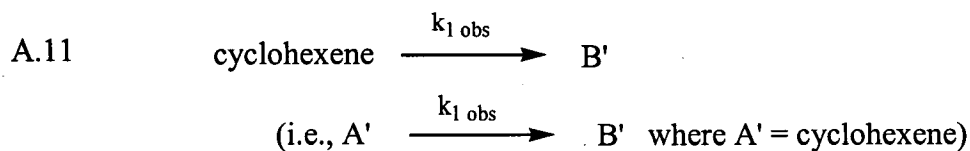
A.9
$$\begin{aligned} \frac{d[C]}{dt} &= k_3[B]^2 \\ &= -\frac{1}{2} \left(\frac{d[A]}{dt} + \frac{d[B]}{dt} \right) \end{aligned}$$

The mass balance equation is A.10

A.10
$$[A]_0 = [A]_t + [B]_t + 2[C]_t$$

(As a check $d[A]_0/dt = 0 = d[A]/dt + d[B]/dt + 2d[C]/dt$, 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 [cyclohexene]₀ and [cyclohexene]_t vs time data into MacKinetics. That is, the actual system numerically integrated is:



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

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

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

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

The mass balance equation A.17 is easily derived by adding $\frac{d[\text{A}']}{dt} + \frac{d[\text{B}']}{dt} + 2\frac{d[\text{C}']}{dt}$, showing

this equals zero, and then integrating (where $[\text{B}]_0 = [\text{C}]_0 = 0$).

$$\text{A.17} \quad [\text{A}]_0 = [\text{A}]_t + [\text{B}]_t + 2[\text{C}]_t \text{ or } [\text{A}]_0 - [\text{A}]_t = [\text{B}]_t + 2[\text{C}]_t$$

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

$$\text{A.3(a)} \quad [\text{cyclohexene}]_0 = [\text{A}']_0 = \frac{1400}{\alpha}[\text{A}]_0$$

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

Combining these equations with A.17 yields:

$$\text{A.18(a)} \quad [\text{A}']_0 - [\text{A}']_t = \frac{1400}{\alpha}([\text{A}]_0 - [\text{A}]_t) = [\text{B}']_t + 2[\text{C}']_t$$

But substituting equation A.10 yields

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

From which it follows that

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

Which leads to the following identities:

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

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

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 $k_{1\text{obs}}$, $k_{2\text{obs}}$, $k_{3\text{obs}}$ and k_1 , k_2 and k_3 .

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

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

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

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

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

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

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:

$$\text{A.22} \quad k_1 = k_{1\text{obs}}$$

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

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

Experimental Methods to Determine y

This section is unchanged from the prior Supporting Information. Note that for the net reaction, $\text{A} \rightarrow (1-y)\text{B} + y\text{C}$ (equation 4 herein), where $y = y(t)$, the estimate of $y = 0.45$ determined on p. 146 elsewhere¹) 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.