

**Reply to Comment on “Fitting and Interpreting Transition-Metal Nanocluster Formation and Other Sigmoidal-Appearing Kinetic Data: A More Thorough Testing of Dispersive Kinetic vs Chemical-Mechanism-Based Equations and Treatments for 4-Step Type Kinetic Data”**

The preceding Comment<sup>1</sup> results from our correction<sup>2</sup> of a communication<sup>3</sup> asserting that 2-empirical parameter dispersive kinetic models (DKMs)<sup>5</sup> can adequately fit—and thus be accounted for via 2 fewer parameters—unusual shape, “4-step” kinetic data for Pt<sub>n</sub> nanoparticle formation and aggregation in solution from Pt(1,5-COD)-Cl<sub>2</sub> plus H<sub>2</sub> and Bu<sub>3</sub>N. In fact, they cannot, as the products, kinetic data and rigorous AICc statistical tests elsewhere unequivocally demonstrate.<sup>2</sup> The AICc statistics also directly disprove the assertion<sup>1</sup> that the 4-step model is “overparameterized”; to the contrary, the enormous evidence ratios observed<sup>2</sup> offer compelling experimental evidence that the 2-parameter DKMs are strongly underparameterized. The failed hypothesis,<sup>1,3</sup> that the DKMs do (or “might”<sup>1</sup>) fit 4-step type data has been disproven.<sup>2</sup> The fundamental flaw in the prior communication<sup>3</sup> and the preceding Comment<sup>1</sup> is their lack of attempted disproof<sup>4</sup> followed by continued efforts to promote<sup>1,3</sup> the failed DKMs hypothesis. Assertions/claims and attempted proof are often the improper scientific basis for those<sup>3</sup> and other papers,<sup>5</sup> a serious flaw that others have also noted.<sup>6</sup> We do not prove in science; we only disprove.<sup>4</sup>

We respond below to the preceding Comment’s remaining assertions/claims in-so-far as the very limited space allows. (1) Assertion:<sup>1</sup> we “failed to acknowledge” DKMs. This is false; it ignores<sup>1</sup> our correction<sup>2</sup> and our paper<sup>7</sup> connecting DKM Avrami *n* and *k* parameters and F–W *k*<sub>1</sub> and *k*<sub>2</sub> rate constants, as well as our review.<sup>8</sup> (2) Assertion: “determining the best kinetic model ... does not

reside solely with a comparison of empirical curve-fits”. We agree completely. This is why the postulated 4-step mechanism for solution nanoparticle nucleation, autocatalytic growth, bimolecular agglomeration and autocatalytic agglomeration<sup>9</sup> considered, and accounts for, the products (nanoclusters, agglomerated nanos and some bulk metal) and the metal, ligand type, concentration, M–L BDE, and other data<sup>9</sup>—all while ruling out 18 alternative mechanisms (plus 3 now disproved DKMs<sup>2</sup>). In dramatic contrast, the disproved<sup>2</sup> DKMs<sup>1,3</sup> do not even account for the observed 4-step products, the erroneous prior communication<sup>3</sup> being based solely on sometimes failed<sup>2</sup> curve-fits to but one data set!<sup>3</sup> The DKMs also fail to explain<sup>3</sup>—much less to have discovered<sup>9</sup>—the 10 total (average<sup>2,9</sup>) physical insights from the 4-step mechanism.<sup>2,9</sup> Moreover, the DKMs have little mechanistic value—despite repeated claims to the contrary<sup>1,3,5</sup>—as expected due to their lack of balanced reactions and admitted<sup>1</sup> empirical “ $\alpha$ ” and “ $\beta$ ” parameters.<sup>1,3,5</sup> Asserted next is (3) that the initially surprising,<sup>9</sup> honestly reported,  $\pm 10^4$  error bars on just *k*<sub>1</sub> (not *k*<sub>2</sub>, *k*<sub>3</sub>, or *k*<sub>4</sub>) of the 4-step mechanism are “simply put, unacceptable”.<sup>1</sup> Conveniently forgotten here are the prior author’s<sup>1</sup> own DKMs’ empirical  $\alpha$  parameter error bars of  $\pm 10^{2-3}$  ( $\alpha = 30 \pm 900$ ;  $30 \pm 1000$ ;  $20 \pm 200^{5c}$ ), a telling insight indicative of the lack of attempted disproof of the DKMs<sup>1,3,5</sup>—models which also fail to give the desired dispersion of rate constants. Available are published (but uncited<sup>1</sup>) reasons that the *k*<sub>1</sub> (and apparently also  $\alpha^{5c}$ ) error bars may more generally be large: hidden and thus uncontrolled experimental variables; large 5-variable curve-fitting error; a (simulation-demonstrated) insensitivity to *k*<sub>1</sub>,<sup>9</sup> and well-known (previously cited<sup>9</sup>), classic problems any time one attempts to deconvolute multiple exponentials by curve-fitting. Multiple unreferenced assertions and failures to cite relevant literature round out the prior Comment:<sup>1</sup> (4) “nucleation and growth are considered to be a single mechanism”. What does this confusing statement actually mean? Why, then, for the implied single step use two words, “nucleation and growth”, and two reaction descriptors?<sup>7</sup> This is a prime example of the key type and source of confusion presently in solid-state kinetics discussed elsewhere<sup>6,7</sup>—not the claimed source of physical insight from DKMs.<sup>1</sup> (5) Next, an incorrect assumption of constant A factors (i.e.,  $\Delta S^\ddagger$  activation parameters)<sup>1</sup> ignores the facts ( $\Delta S^\ddagger_1 = -36(3)$  e.u. and  $\Delta S^\ddagger_2 = -13(6)$  e.u.);  $\Delta S$  is not constant. The concept of  $\Delta H$  and  $\Delta S$  compensation is also ignored,<sup>10</sup> as is the fact that kinetically competing parallel reactions (as underlies DKMs!) must have comparable  $\Delta G^\ddagger$  values. Asserted next is (6) “my dispersive kinetics models contain only two empirical fit parameters”.<sup>1</sup> However, they do not fit the data to even  $\pm 10^{3-4}$  in either of the 2

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parameters (e.g., Figure 3:<sup>2</sup> using eq 2, “ $\alpha = 450 \pm 570000$ ;  $\beta = 1.9 \times 10^{-6} \pm 0.0023$ ”, and eq 3, “ $\alpha = 100 \pm 310000$ ;  $\beta = 8.7 \times 10^{-7} \pm 0.0027$ ”)—results that are, “simply put, unacceptable”,<sup>1</sup> especially since only 2 (not 4) parameters (plus the residual in each case) are being determined. The misuse of Ockham’s razor<sup>11</sup> (my models are “simpler and thus more probable”—not if they do not fit any of the product or kinetic data!) should also be noted.<sup>1,3,5</sup>

Growing, independent evidence for the underlying steps<sup>12,13</sup> of the minimalistic, Ockham’s-razor-based<sup>9,13</sup> 4-step mechanism—especially for its novel, size focusing  $B + C \rightarrow 1.5C$  autocatalytic agglomeration

step<sup>15,16</sup>—is accumulating, independent: XAFS,<sup>14</sup> in situ TEM,<sup>15</sup> XANES and SAXS work,<sup>16</sup> and catalysis-based kinetic evidence.<sup>17</sup> Nevertheless, needed next is a chemical mechanism *more detailed* than the 4-step model which can also account for the nanoparticle size distribution data.<sup>9,12,13,16</sup> Recent, elegant XANES and SAXS work that provides direct evidence for size distributions versus time—and for a 4-step mechanism—is an important effort in the right direction.<sup>16</sup>

**Eric E. Finney and Richard G. Finke\***

*Department of Chemistry, Colorado State University,  
Fort Collins, Colorado 80523*

*Received December 30, 2009. Revised Manuscript Received January 28, 2010*

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