

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 Comment¹ results from our correction² of a communication³ asserting that 2-empirical parameter dispersive kinetic models (DKMs)⁵ can adequately fit—and thus be accounted for via 2 fewer parameters—an unusual shape, “4-step” kinetic data for Pt_n nanoparticle formation and aggregation in solution from Pt(1,5-COD)-Cl₂ plus H₂ and Bu₃N. In fact, they cannot, as the products, kinetic data and rigorous AICc statistical tests elsewhere unequivocally demonstrate.² The AICc statistics also directly disprove the assertion¹ that the 4-step model is “overparameterized”; to the contrary, the enormous evidence ratios observed² offer compelling experimental evidence that the 2-parameter DKMs are strongly underparameterized. The failed hypothesis,^{1,3} that the DKMs do (or “might”¹) fit 4-step type data has been disproven.² The fundamental flaw in the prior communication³ and the preceding Comment¹ is their lack of attempted disproof⁴ followed by continued efforts to promote^{1,3} the failed DKMs hypothesis. Assertions/claims and attempted proof are often the improper scientific basis for those³ and other papers,⁵ a serious flaw that others have also noted.⁶ We do not prove in science; we only disprove.⁴

We respond below to the preceding Comment’s remaining assertions/claims in-so-far as the very limited space allows. (1) Assertion:¹ we “failed to acknowledge” DKMs. This is false; it ignores¹ our correction² and our paper⁷ connecting DKM Avrami *n* and *k* parameters and F-W *k*₁ and *k*₂ rate constants, as well as our review.⁸ (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 agglomeration⁹ considered, and accounts for, the products (nanoclusters, agglomerated nanos and some bulk metal) and the metal, ligand type, concentration, M-L BDE, and other data⁹—all while ruling out 18 alternative mechanisms (plus 3 now disproved DKMs²). In dramatic contrast, the disproved² DKMs^{1,3} do not even account for the observed 4-step products, the erroneous prior communication³ being based solely on sometimes failed² curve-fits to but one data set!³ The DKMs also fail to explain³—much less to have discovered⁹—the 10 total (average^{2,9}) physical insights from the 4-step mechanism.^{2,9} Moreover, the DKMs have little mechanistic value—despite repeated claims to the contrary^{1,3,5}—as expected due to their lack of balanced reactions and admitted¹ empirical “ α ” and “ β ” parameters.^{1,3,5} Asserted next is (3) that the initially surprising,⁹ honestly reported, $\pm 10^4$ error bars on just *k*₁ (not *k*₂, *k*₃, or *k*₄) of the 4-step mechanism are “simply put, unacceptable”.¹ Conveniently forgotten here are the prior author’s¹ own DKMs’ empirical α parameter error bars of $\pm 10^{2-3}$ ($\alpha = 30 \pm 900$; 30 ± 1000 ; 20 ± 200 ^{5c}), a telling insight indicative of the lack of attempted disproof of the DKMs^{1,3,5}—models which also fail to give the desired dispersion of rate constants. Available are published (but uncited¹) reasons that the *k*₁ (and apparently also α ^{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*₁,⁹ and well-known (previously cited⁹), 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:¹ (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?⁷ This is a prime example of the key type and source of confusion presently in solid-state kinetics discussed elsewhere^{6,7}—not the claimed source of physical insight from DKMs.¹ (5) Next, an incorrect assumption of constant A factors (i.e., ΔS^\ddagger activation parameters)¹ ignores the facts ($\Delta S^\ddagger_1 = -36(3)$ e.u. and $\Delta S^\ddagger_2 = -13(6)$ e.u.); ΔS is not constant. The concept of ΔH and ΔS compensation is also ignored,¹⁰ as is the fact that kinetically competing parallel reactions (as underlies DKMs!) must have comparable ΔG^\ddagger values. Asserted next is (6) “my dispersive kinetics models contain only two empirical fit parameters”.¹ 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 3:² using eq 2, “ $\alpha = 450 \pm 570000$; $\beta = 1.9 \times 10^{-6} \pm 0.0023$ ”, and eq 3, “ $\alpha = 100 \pm 310000$; $\beta = 8.7 \times 10^{-7} \pm 0.0027$ ”)²—results that are, “simply put, unacceptable”,¹ especially since only 2 (not 4) parameters (plus the residual in each case) are being determined. The misuse of Ockham’s razor¹¹ (my models are “simpler and thus more probable”¹—not if they do not fit any of the product or kinetic data!) should also be noted.^{1,3,5}

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

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step^{15,16}—is accumulating, independent: XAFS,¹⁴ in situ TEM,¹⁵ XANES and SAXS work,¹⁶ and catalysis-based kinetic evidence.¹⁷ Nevertheless, needed next is a chemical mechanism *more detailed* than the 4-step model which can also account for the nanoparticle size distribution data.^{9,12,13,16} 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.¹⁶

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