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Analysis of Samples for the ICTAC Lifetime-Prediction Round-Robin Exercise

A. K. Burnham

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Alan K. Burnham
Energetic Materials Center
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, CA 94551

Abstract

Derivation of chemical kinetic models for prediction of material and component lifetimes is of broad interest and value. This work analyzes data that was distributed to me, among others, by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) as part of a blind study of kinetic analysis. The results from this report will be combined with results from other parties to create a broader comparison of kinetic analysis methods. In addition to the eight ICTAC data sets, which appear to contain one set of simulated data, presumably for ground truth comparison, I created an additional simulated data set to compare the reliability of isoconversional and model-fitting approaches. It is usually possible to fit the data well with both isoconversional and model fitting approaches, although the isoconversional method is usually faster and provides better fits to the data, particularly for complex reaction profiles. The two methods often, but not always, give similar predictions. Predictions of the isoconversional model will fail to the extent that the reaction contains competitive or crossing-concurrent reaction characteristics. Model fitting will either do better or worse depending on how well the derived model includes the appropriate characteristics, and the probability of deriving a good model depends both on the sophistication of the modeling software and the skill of the analyst.

Introduction

The derivation of kinetic parameters from nonisothermal experiments has a long and controversial history. As originally practiced, including by me between 20 and 30 years ago, the kinetic parameters were typically extracted from a single experiment at one heating rate. A practice developed in the thermal analysis community to fit a spectrum of models (e.g., those contained in a review by Brown et al.[1]) This practice was attacked head-on by Sergey Vyazovkin and coworkers in a series of papers,[2,3] who promoted the use of an advanced isoconversional method using multiple heating rates as a fast and easy way to derive an accurate and flexible fit to complex reaction profiles. Isoconversional methods date back to the early 1960s, but Vyazovkin updated the mathematics and promoted the use of the method as "model-free" kinetics.[4]

The origin of the term "model free" was in response to the invalid, single heating-rate, model-fitting procedure that had become so common. On the other hand, it must be remembered that all isoconversional methods assume that the reaction sequence does not

change as a function of temperature or heating rate. This assumption can fail for at least two situations: (1) competing reactions with different activation energies, and (2) concurrent reactions with sufficiently different activation energies so that which one is faster changes over the range temperature range of interest. It is also a questionable assumption for sequential reactions with greatly different activation energies, for which the rate limiting step changes with temperature, not conversion.

It should also be recognized that model fitting to multiple thermal histories has been practiced for at least 20 years, including by me, so dismissal of all model fitting approaches is not correct either. A reasonable perspective on valid and invalid kinetic analysis approaches was given in a previous ICTAC study of kinetic analysis, in which I participated.[5] A major conclusion of the study, stated weakly in the abstract, was that all multiple heating rate methods were fairly successfully. Consequently, both isoconversional and multi-thermal-history model fitting methods should be considered as acceptable approaches. My paper was more direct: any approach that uses only a single heating rate should not be considered as either acceptable or publishable.[6]

Even though both isoconversional and model-fitting analyses of multiple heating rates have the potential to derive accurate and useful kinetic parameters, it is not certain that they will for any particular data set. As mentioned earlier, some complex reactions may not honor the isoconversional criterion, so predictions outside the range of calibration can be significantly in error. Likewise, calibration of a model over a relatively narrow range of thermal histories may not be able to distinguish between two different models that perform quite differently outside the range of calibration. The sophistication of the analysis software and the skill of the analyst are more important in this case, but even the best can fail when the data is noisy and over a limited range and the extrapolation is long.

I have used the isoconversional method in the AKTS Thermokinetics program[7,8] and both isoconversional and model-fitting methods in the LLNL Kinetics05 program to analyze the data sets provided in the ICTAC lifetime prediction exercise. My analysis indicates that some data sets are well behaved, in that parameters and predictions of several approaches are very similar. However, other data sets have characteristics that lead to differences in predictions of different analysis methods, and which prediction is more correct cannot be answered without additional information. I also created one additional data set involving both competitive and consecutive reactions that shares superficial characteristics of some of the experimental data sets, and I compare the predictions of various models with ground-truth calculations directly from the model.

Kinetic Models

The simplest and most common kinetic model is the nth-order model

$$d(1-\alpha)/dt = - k (1-\alpha)^n \qquad (1)$$

where α is the fraction converted, t is time, and $k=A\exp(-E/RT)$, where A is the frequency factor, E is the activation energy, R is the gas constant, and T is temperature. The reaction parameter n is commonly unity, giving a first-order model. Both the AKTS Thermokinetics and LLNL Kinetics05 programs use the Friedman isoconversional method, in which an Arrhenius plot of the instantaneous rate, in units of fraction reacted per unit time, is made at each selected fraction reacted for experiments with different thermal histories:

$$\ln(-d(1-\alpha)/dt = -E/RT + \ln(A(1-\alpha)^n) \qquad (2)$$

in which n is the reaction order, T is the temperature for any particular experiment, t is time, and. In practice, if the interval between conversion points is small, the dependence on reaction order can be ignored for that interval, and the dependence of reaction rate on conversion, or form factor, is absorbed into the instantaneous A values.

A chemical reaction model in Kinetics05 that I often find useful is an extended Prout-Tompkins (nucleation-growth) model:

$$d(1-\alpha)/dt = k (1-\alpha)^n(1-q(1-\alpha))^m \qquad (3)$$

where q is an initiation parameter and m is a nucleation-growth parameter related to the dimensionality of growth. If n=0 and m=1, Eq (3) has the limit of the linear chain branching model. If n=1 and m=0, it has the limit of a first-order reaction. In n=m=1, it is the standard Prout-Tompkins model.

Kinetics05 has the ability to fit up to three parallel nucleation-growth reactions. It can also fit up to three parallel nth-order reactions, each of which can have a Gaussian distribution of activation enerties. Finally, it has the ability to fit up to 25 parallel first-order reactions. For the latter, the A can be a constant or it can follow the relationship $\ln(A) = A_o + \ln(E)$.

Another reaction model in Kinetics05 that was not used for fitting but was used to create another simulated data set is the alternate pathway model, in which components X, Y, and Z have the following reaction pathways: X to Y, Y to Z, and X to Z. In each case the rate constant is an nth-order reaction having a Gaussian distribution of activation energies, which gives a distribution of rate constants for each reaction.

Results

Sample 1

This data set appears to be created by simulation. No baseline correction appears to be necessary, and none was made for the Kinetics05 analyses, but the baseline of negligible reaction is not long enough for the AKTS program to come to that conclusion automatically. There appear to be inflection points corresponding to multiple reactions in the reaction profile, and the width of the reaction profile is twice as large as that expected for a first-order reaction consistent with the activation energy derived from shift in T_{max} by Kissinger's method (50.27 kcal/mol) or by the corresponding energy derived from the 50% conversion point (43.67 kcal/mol). In fact, the width of the reaction profile decreases from 40 to 35 ^{o}C as the heating rate increases, which suggests multiple parallel reactions that are converging towards a common T_{max} as the heating rate increases.

Isoconversional kinetic analysis by both the AKTS Thermokinetics and LLNL Kinetics05 programs indicate that the activation energy increases during the course of the reaction, as shown in Figure 1. The AKTS results appear rather erratic during the first and last 10% of the reaction, probably because of the code's attempt to optimize the baseline. The simulated data was truncated either just before or just about the end of the reaction, and the AKTS code appeared to want to use the last several points at the high temperature range to make a sloped baseline. I ran three cases with the AKTS code, choosing different initial baselines with slightly different results, but the values presented here chose an initial flat baseline. A comparison of "measured" and calculated rates are given in Figures 2 and 3 for the two codes. For both programs, the calculated and "measured" reaction rates overlay, and the same is true for the fractions converted (not shown).
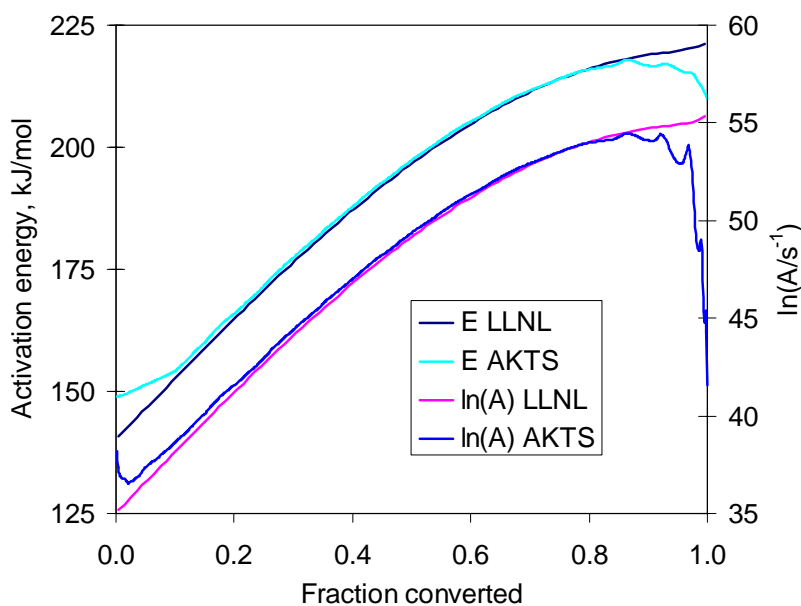

Figure 1. Comparison of isoconversional analysis of Sample 1 data using the LLNL Kinetics05 and AKTS Thermokinetics software.
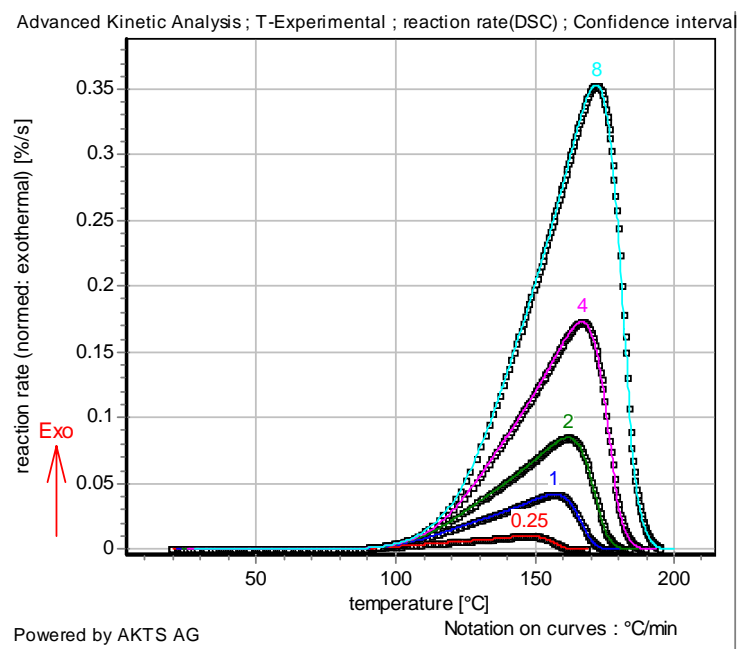
Figure 2. Comparison of "measured" and calculated reaction rates for Sample 1 data using the AKTS Thermokinetics program. The numbers above the curves are the heating rates in °C/min.
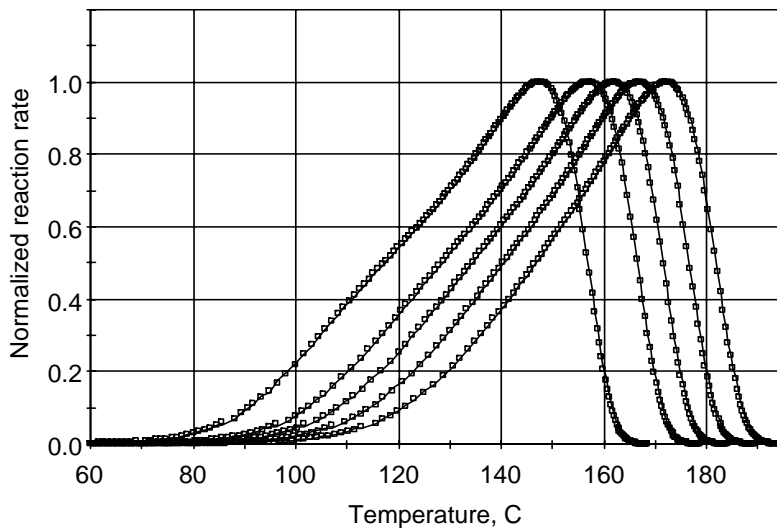

Figure 3. Comparison of "measured" (open squares) and calculated (lines) reaction rates for Sample 1 from the LLNL Kinetics05 program. The heating rates, from left to right, are 0.25, 1.0, 2.0, 4.0, and 8.0 °C/min.

There is a growing opinion within the thermal analysis community that isoconversional analysis can obtain substantially better fits than can model fitting. That is certainly true in some cases, but not in all. For comparison, the sample 1 data were fitted to two separate models. One is a discrete-activation-energy-distribution model, in which

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ln(A)=A$_o$+bE, and a second model contains three parallel nth-order reactions. The comparison between measured and calculated reaction rates for these two models is given in Figure 4. The quality of the fits is also very good—the differences between data and calculation are different in detail yet comparable in any practical sense. The sum of squared residual between measured and calculated fractions converted are 0.00174 for the three parallel nth-order reaction, 0.0075 for the discrete activation energy distribution model, and 0.00002 for the isoconversional model. The isoconversional method has lower residuals because of its greater number of parameters, but it is not obvious that the improvements would give any advantage in application if there weren't some other important different in extrapolation outside the range of calibration. The three parallel nth-order reactions are beginning to be resolved at the lowest heating rate.

The reaction parameters for these two models are as follows.

Discrete model:
ln(A)=4.4841+0.2274*E(kJ/mol)
2.14%@125.59, 3.76%@133.17, 6.27%@141.76, 6.06%@150.34,
7.80%@158.93, 8.02%@167.51, 5.27%@176.10, 14.95%@184.69,
5.52%@201.86, and 40.21%@210.45.

Parallel nth-order model:
19.2% with A=5.47×10^{15}, E=139.44 kJ/mol, n=1.45
33.6% with A=1.64×10^{18}, E=166.10 kJ/mol, n=1.31
47.2% with A=5.52×10^{22}, E=210.06 kJ/mol, n=1.03

It is interesting that the highest energy reactions in both models have similar fractions and very close activation energies. For comparison, the isoconversional activation energy from Kinetics05 increases to 221.2 kJ/mol at high conversion.

The end product of the kinetic analyses is not the kinetic parameters themselves but a prediction of the extent of reaction at far longer times and lower temperatures than the calibration data sets from which the kinetics were obtained. This is a fairly common problem in applications where lifetime prediction is needed. Thermal histories prescripted by ICTAC are 3 years at 25, 50, and 80 ^{o}C, and 3 years at 25 and 50 ^{o}C with diurnal variations of 10 and 30 ^{o}C, respectively. Predictions for these four fitting approaches to the Sample 1 data are given in Table 1. The predictions are very close, except the AKTS model appears to predict too low of conversions for the 25 ^{o}C cases.
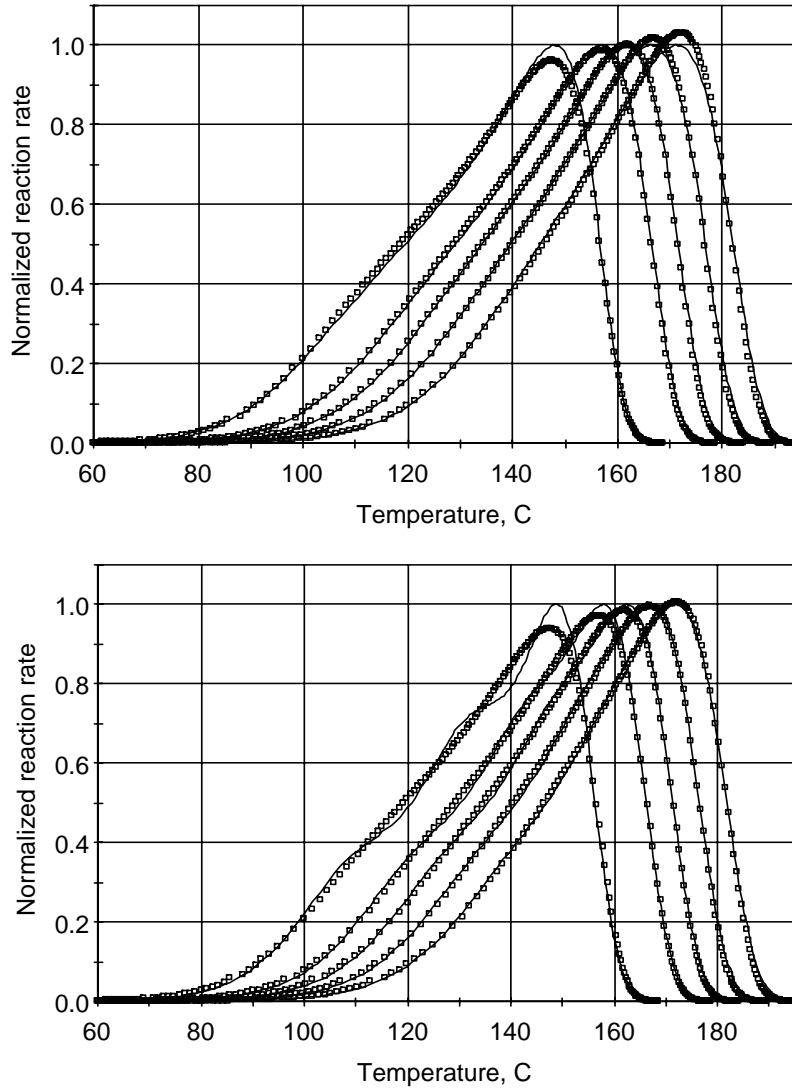
Figure 4. Comparison of measured (open squares) and calculated (lines) reaction rates for the discrete activation energy (top) and parallel nth-order reaction (bottom) models derived by Kinetics05.

Table 1. Predictions of the four Sample 1 models for three years at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
AKTS isoconv	0.90	24.14	71.85	2.67	54.00
LLNL isoconv	3.11	24.97	72.62	5.19	54.43
LLNL discrete	4.51	24.80	70.43	6.49	52.95
LLNL 3-nth	3.27	25.47	69.56	5.67	54.50

Sample 2

Sample 2 is an energetic material with at least two exothermic processes contributing to the DSC signal provided. The kinetics of the sample were determined by the isoconversional method using the AKTS Thermokinetics and LLNL Kinetics05 programs and by fitting two parallel, extended Prout-Tompkins, nucleation-growth reactions using Kinetics05.

The A and E values from various isoconversional analyses are compared in Figure 5. Two different results are given for the AKTS program using different baseline intervals. Overall, the A and E values from Thermokinetics agree well with those from Kinetics05 except for the first and last several percent. This is due to the differences in baseline corrections for the two programs, which affects the initial and final kinetic parameters especially.

The corresponding comparisons of measured and calculated rates are shown in Figure 6 for Thermokinetics and in Figure 7 for Kinetics05. In Figure 6, the wider temperature interval in the right hand fit (AKTS2) gives less erratic AE pairs at low and high conversions, and the predictions are probably more reliable. Figure 8 shows the fit to two parallel nucleation-growth reactions using Kinetics05. The agreement between measured and calculated values is comparable to that using the isoconversional method. The reaction parameters for the parallel nucleation-growth reactions are:

$\quad$ 90% with A=3.06×10^{12} s^{-1}, E=129.7 kJ/mol, m=1.00, n=1.40
$\quad$ 10% with A=6.00×10^{12} s^{-1}, E=138.1 kJ/mol, m=1.00, n=1.00

One distinctive difference between the Thermokinetics and Kinetics05 fits are that the former appear essentially perfect. This is deceptive, because the Thermokinetics program modifies the data in its optimization procedure via a complex baseline correction so that it conforms to the isoconversional assumption. If the isoconversional assumption is perfectly valid, that will result in a better fit, but the true comparison between measured and calculated values is lost. The Kinetics05 program has only a manual baseline correction routine, and no further changes to the measured results are made during kinetic parameter determination. Inspection of the reaction profiles in the Kinetics05 plots suggests that the character of the reaction profile is changing with heating rate, so it is quite possible that the isoconversional assumption is not perfectly valid. Then again, it is possible that the parallel-reaction model is not perfectly valid, either.

A comparison of predictions from the four sets of kinetic parameters is given in Table 2. Due to the initial high activation energies in the AKTS isoconversional fits, the predicted conversions at low temperature are significantly lower. However, they do agree reasonably well with the predictions from the nucleation-growth model fit. The Kinetics05 isoconversional and nucleation predictions are between the two Thermokinetics predictions for the modulated 50 ^{o}C condition, and all models give essentially the same prediction at 80 ^{o}C.
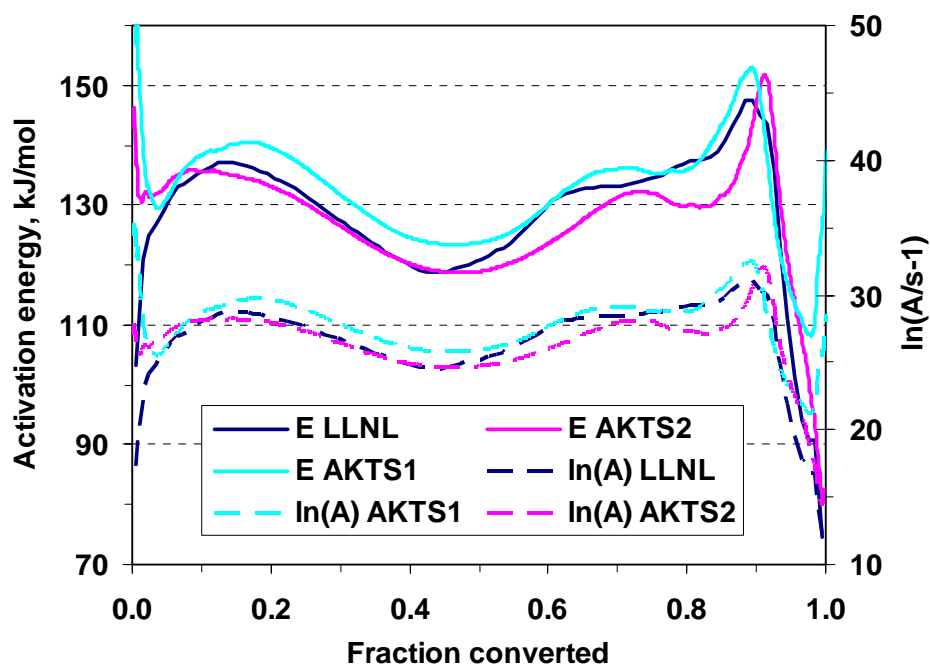
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Figure 5. Isoconversional kinetic parameters from the AKTS Thermokinetics and LLNL Kinetics05 programs. The two AKTS parameter sets use different temperature intervals as shown in Figure 6.
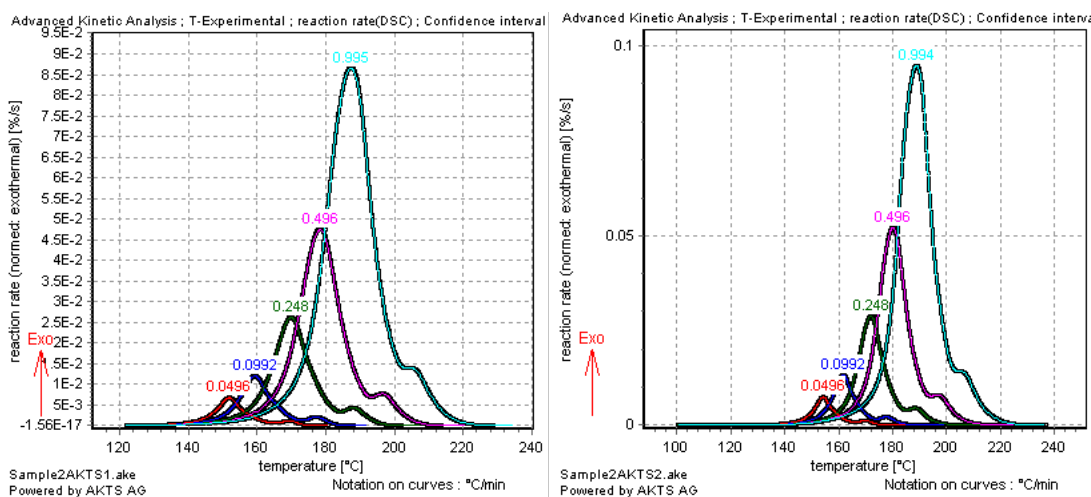

Figure 6. Two different fits of the Sample 2 data using different temperature intervals in the AKTS Thermokinetics program. The number above each curve is the heating rate in °C/min.
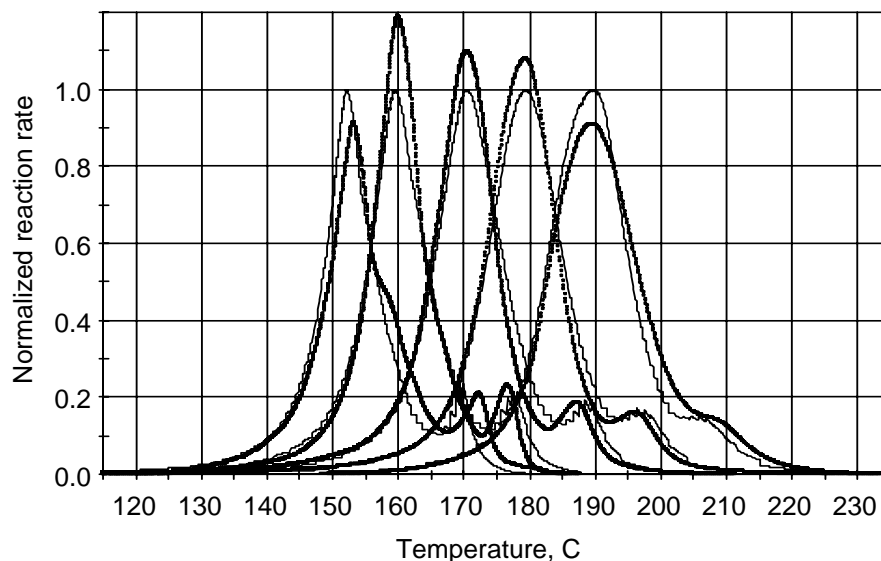
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Figure 7. Comparison of measured (points) and calculated (thin lines) reaction rates for the isoconversional kinetic analysis of Sample 2 using the LLNL Kinetics05 program. The heating rates from left to right are 0.05, 0.1, 0.25, 0.5, and 1.0 ^{o}C/min.
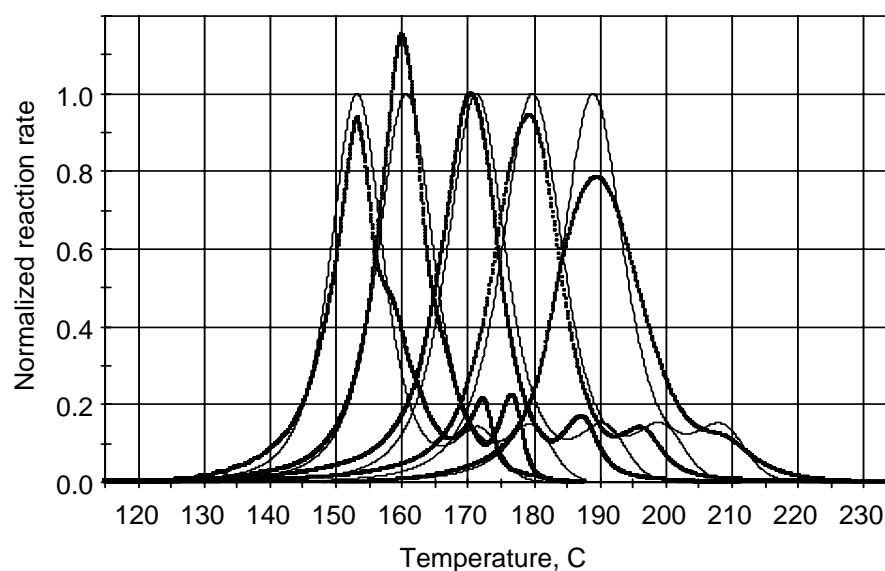
Figure 8. Comparison of measured and calculated reaction rates for two parallel nucleation-growth reactions using the LLNL Kinetics05 program.

Table 2. Predictions of the four Sample 2 models for three years at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
AKTS isoconv1	0.014	0.89	90.72	0.04	35.9
AKTS isoconv2	0.004	0.89	87.2	0.02	17.61
LLNL isoconv	0.28	2.67	88.74	0.43	27.02
LLNL 2-nuc-gr	0.005	0.33	89.83	0.009	20

Sample B3

Sample B3 provides the most interesting discrepancy between AKTS Thermokinetics and LLNL Kinetics05 results. The activation energy versus conversion curves for five different isoconversional analyses are shown in Figure 9. The analyses all have an activation energy near 150 kJ/mol in the 5-15% conversion range, but the Thermokinetics curves tend to start lower at very low conversions. At higher conversions, the Kinetics05 results depend heavily on the type of baseline correction made (linear or curve plus sigmoid). Two Thermokinetics analyses with slightly different temperature cuts give very similar results up to 70% conversion but then undergo different oscillations. To confirm that these differences depend mostly on the nature of the baseline correction, the Thermokinetics program was used to analyze the same files created using the nonlinear baseline correction in Kinetics05. The activation energies and frequency factors were very similar to those from Kinetics05.

Because the baseline correction is so critical in this case, it is useful to show the raw data. This is done in Figure 10. The scale of the heat flow has been adjusted for each sample by a factor roughly proportional to the inverse of the heating rate so the curves are more clearly visible. The baseline is obviously curved, and there may be some additional displacement during conversion due to a change in the heat capacity of the sample. There is evidence for at least five distinct reactions: two unresolved reactions in the first peak, one in a second large peak, one in a third small peak, and one in a fourth very small peak. Kissinger kinetic analysis of the four peaks give activation energies of 156, 149, 146, and 158 kJ/mol. This suggests that the correct isoconversional analysis should give a relatively constant activation energy near 152 kJ/mol, which is somewhere between the LLNL linear baseline and AKTS2 analyses.
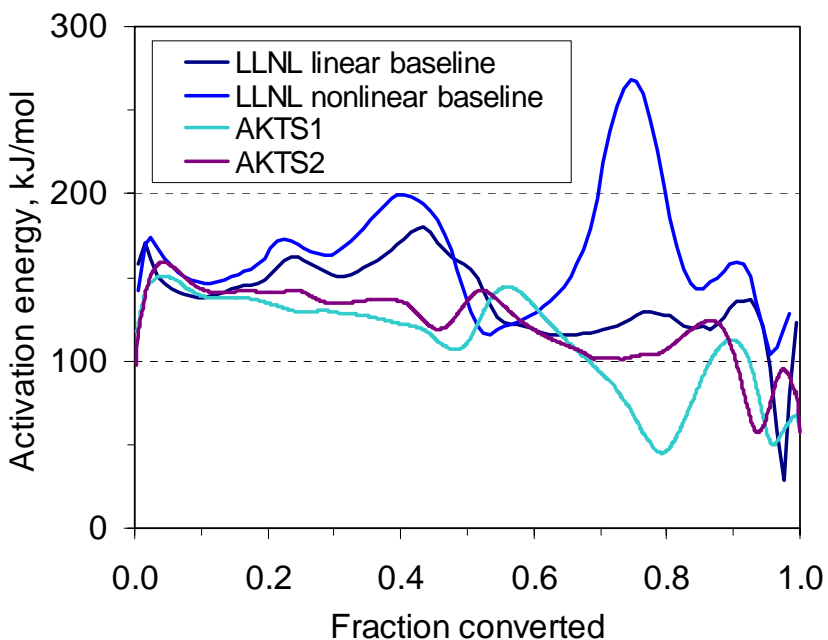

Figure 9. Comparison of activation energy versus conversion for five different isoconversional analyses of Sample B3 DSC data.
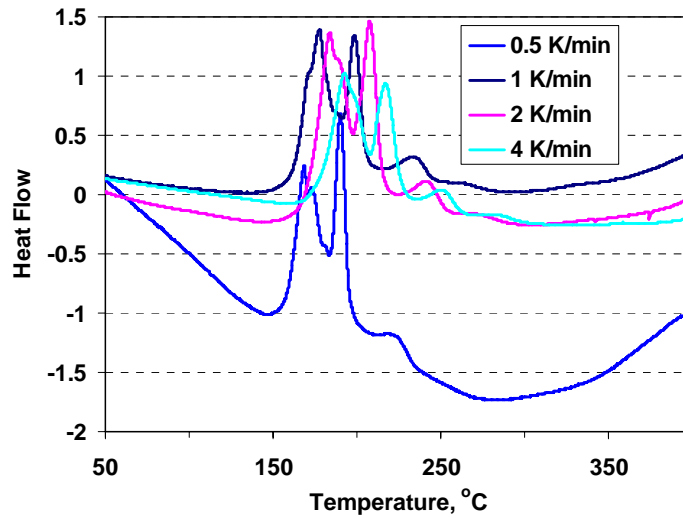
Figure 10. Raw data for Sample B3 showing the curved baseline.

A comparison of measured and calculated rates for the fits are shown in Figures 11 and 12. Again, AKTS Thermokinetics superficially provide an essentially perfect fit, while the isoconversional calculation in Kinetics05 has numerical noise, probably from violation of the isoconversional principle in the data set. However, a close inspection of the 1 °C/min reaction profile in the Thermokinetics plot indicates that the shoulder that was initially on the low temperature side of the first peak has switched to the high temperature side to conform to the other peak profiles. This serves as a reminder that the baseline correction and optimization that forces the data to conform to the isoconversional principle often significant alters the shape of the reaction profile, so the agreement between data and calculation in Figure 11 is somewhat misleading.
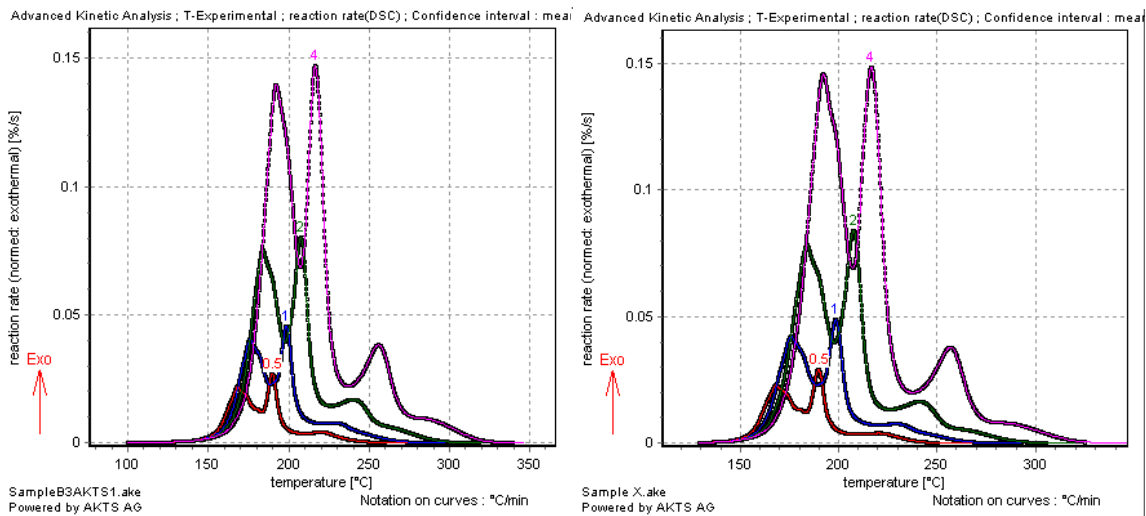

Figure 11. Comparison of measured and calculated rates to two different temperature cuts using the AKTS Thermokinetics program: left=AKTS1 and right=AKTS2
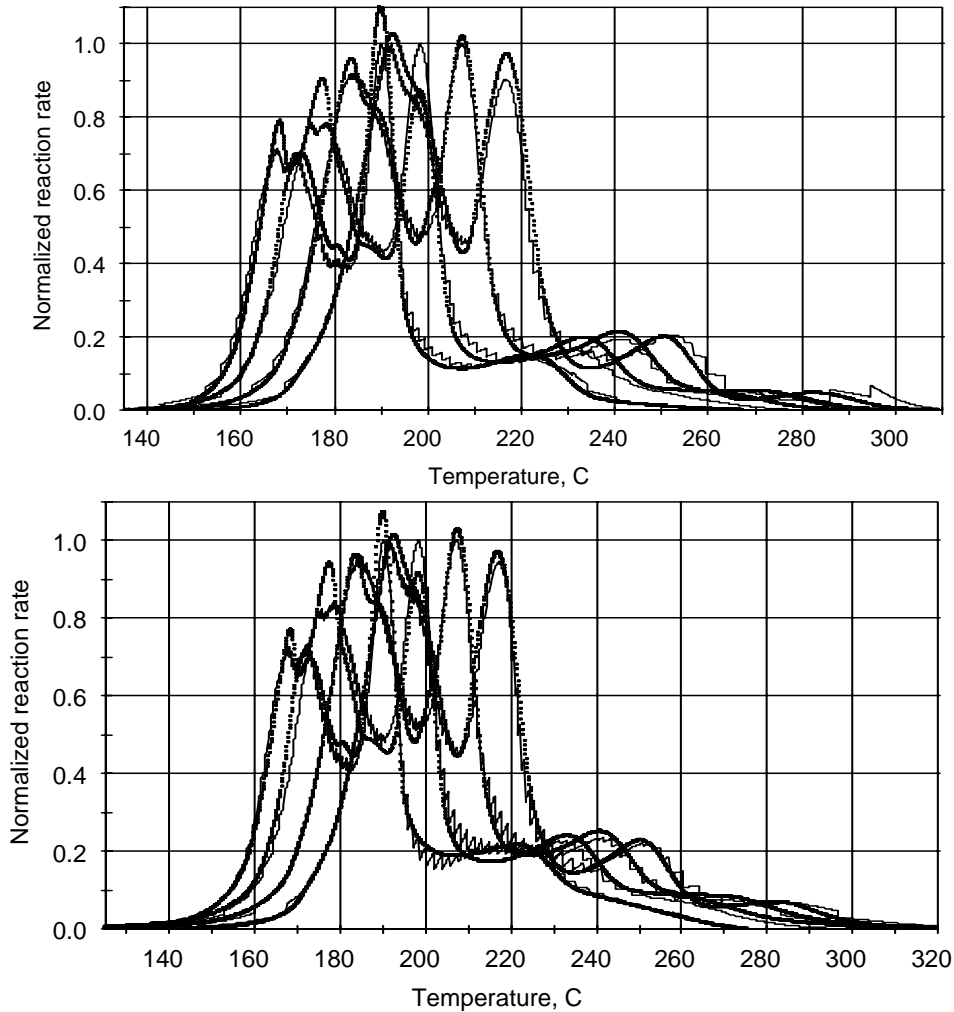
Figure 12. Comparison of measured (points) and calculated (thin lines) reaction rates for Sample B3 from isoconversional analysis by Kinetics05. The top figure used a linear baseline correction, and the bottom figure used a nonlinear baseline correction. Heating rates from left to right are 0.5, 1.0, 2.0 and 4.0 $^{\circ}$C/min.

Another insight into the possible dependence of activation energy on conversion is given by a fit of three independent, concurrent, nucleation-growth reactions using Kinetics05. Although four reactions are readily apparent, three is the maximum that can be used. A partial work-around is to use a high reaction order on the third concurrent reaction to simultaneously fit in an approximate manner the third and fourth peaks. This is adequate if the primary interest is in conversions less than 50%, which would be true for energetic materials. The resulting fit and kinetic parameters are given in Figure 13. The fit is not as good as the isoconversional model, but it is not too bad, either.

The next issue is the predicted fractions converted at the specified thermal histories. These are given in Table 4. The Thermokinetics model predictions are similar to each other, and the Kinetics05 model predictions are also similar to each other. However, the two programs are significantly different from each other, which according to earlier results, can be traced to differences in baseline corrections.
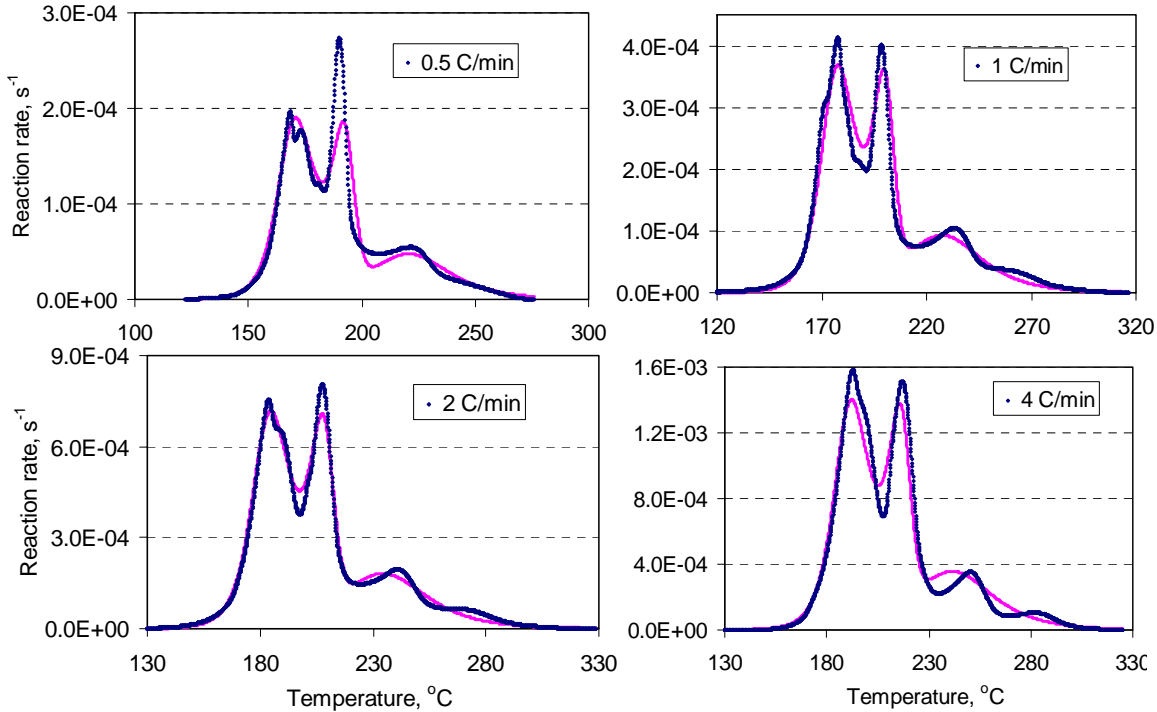
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Figure 13. Comparison of measured (blue) and calculated (magenta) reaction rates for Sample B3 fitted to three parallel nucleation-growth reactions using Kinetics05.

Table 3. Rate parameters for the model fit to Sample B3 data given in Figure 13.

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.522	1.65×10^{16}	160.96	0.60	2.0
0.231	1.22×10^{15}	157.83	0.78	1.0
0.247	6.41×10^{15}	198.13	0.00	2.4

Table 4. Predictions of the five Sample B3 models for three years at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
AKTS isoconv1	0.0035	0.22	90.45	0.02	32.30
AKTS isoconv2	0.0035	0.22	90.94	0.02	36.25
LLNL isoconv1	0.0007	0.09	38.13	0.002	2.02
LLNL isoconv2	0.005	0.45	24.67	0.01	2.47
LLNL 3-nuc-gr	0.0003	0.04	26.06	0.0001	2.29

To better understand the results in Table 4, it is useful to plot the fraction converted as a function of time at 80 ^{o}C for all five models. In order to obtain more complete reaction, the simulation is done for 10 years rather than 3 years. One can see in Figure 14 that the form of the reaction is similar, particularly for the four isoconversional models, but the LLNL lifetime predictions are significant longer. This is a direct result of the higher activation energies (and corresponding frequency factor) in the 15-50% conversion range in Figure 9. Note that the predictions for the first 30% of conversion are very similar for the Kinetics05 isoconversional and 3-parallel nucleation-growth models.
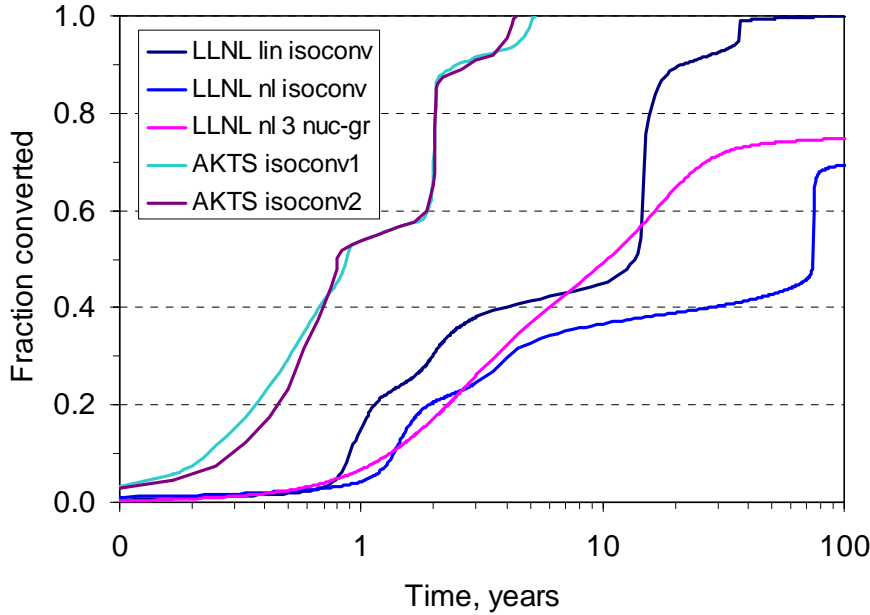
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Figure 14. Comparison of aging predictions at 80 $^{\circ}$C for the five models for Sample B3 given in Table 4.

The obvious question is which is most correct? This can only be decided by real aging experiments. However, I do have reservations about both the data and all analyses that I would address by additional short-term experiments if it were my sample and task to make the prediction:

[1] I would use a larger sample at the lowest heating rate to reduce the magnitude of curvature one needs to address in the baseline correction. If there are concerns about the change in the course of the reaction due to samples size, I would point out that gaseous diffusion and chemical decomposition have different activation energies, so those would be held more constant if sample size were scaled with heating rate, anyway.

[2] I would rerun the sample at 1 $^{\circ}$C/min, since the first peak has a qualitatively different fine-structure. If the difference is fine structure is reproducible, some other factor should be considered that may be causing the breakdown of the isoconversional principle.

[3] I would run at least one nominally isothermal condition, and possibly two, to break the degeneracy of different models under linear heating conditions. To minimize the effect of any thermal transient, I would heat the sample at 1 $^{\circ}$C/min to 140 and 160 $^{\circ}$C to check the correspondence between predicted measured induction times. After waiting some appropriate number of hours, one could continue the ramp at 1 $^{\circ}$C/min to some final temperature of about 300 $^{\circ}$C to assure that the correct total enthalpy is being obtained. The difference in predictions is much greater at 140 than 160 $^{\circ}$C, but the time scale has increased from several hours to a few days. If reaction progress becomes difficult to monitor by heat flow at that temperature, use of an alternate technique such as weight loss could be useful.

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In fact, such an isothermal test as proposed in [3] has reported by Roduit et al.[8] and may well be a yet-to-be-revealed part of this exercise.   In that case, a long induction time with a sudden runaway was observed. Runaway can occur for reasons of chemical mechanism, thermal transport, or both. Chemical mechanistic reasons include depletion of stabilizer and buildup of a critical radical concentration. Thermal runaway can occur even for simple first-order reactions if exothermic heat cannot be dissipated, but the sharpness can be amplified if there is a chemical mechanistic reason for acceleration, also. Insufficient information is given in that paper about experimental conditions to understand the role of thermal runaway in his case, but correspondence with him indicates that the runaway is primarily driven by a change in chemical mechanism. If so, this result is more profound than apparently realized. It really has little to do with the goodness of fit, per se, since it is possible to get just as good of fits with enough concurrent reactions. However, the predictions of concurrent and sequential models, of which the isoconversional approach is a special case, can be substantially different.

Sample 4

Figure 15 shows that the dependence of A and E on conversion is similar from the Thermokinetics and Kinetics05 programs, except that the AKTS code peaks later and does not drop as much at high conversion. Again, this is related to the baseline correction and the degree to which the skewness of the reaction profile changes with heating rate. The Kinetics05 program clearly has a larger high-temperature shoulder for the fastest heating rate. Because this correction is manual in Kinetics05, it is possible to come closer to the AKTS result with additional baseline correction trials, but the purpose of this study was to do replicates of what appeared reasonable at the time and compare it to the optimized baseline correction in the other code.

A comparison of measured and calculated reaction rates are shown in Figures 16 and 17 for the isonversional models determined by the AKTS Thermokinetics and LLNL Kinetics05 programs. Again, the Thermokinetics fit is essentially perfect because of the way the data is modified to conform to the isoconversional principle. The LLNL fits show the data closer to the as-collected form, and the change in skewness from low to high heating rates is more obvious.
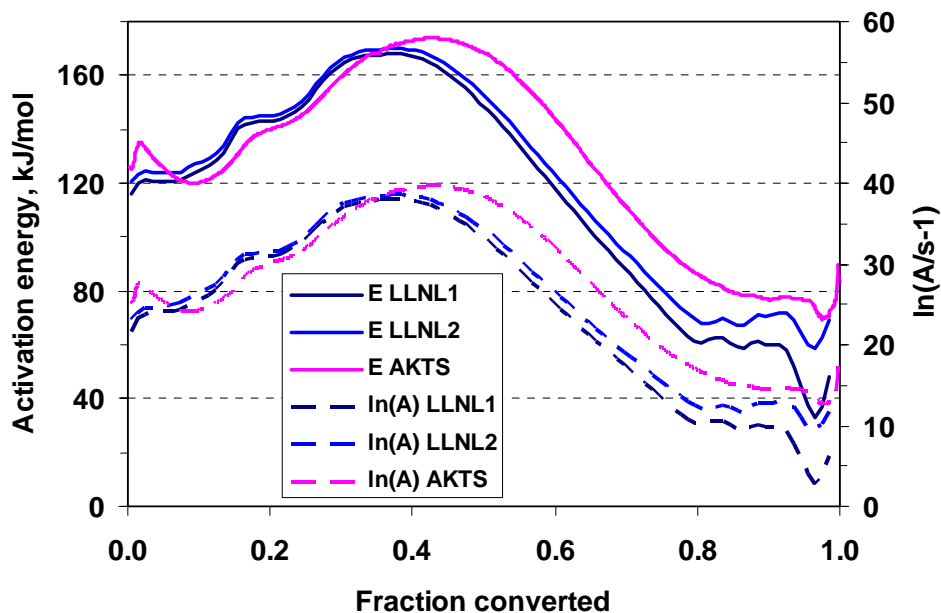
Figure 15. Dependence of activation energy and frequency factor for Sample 4 as determined by the AKTS Thermokinetics and LLNL Kinetics05 programs.
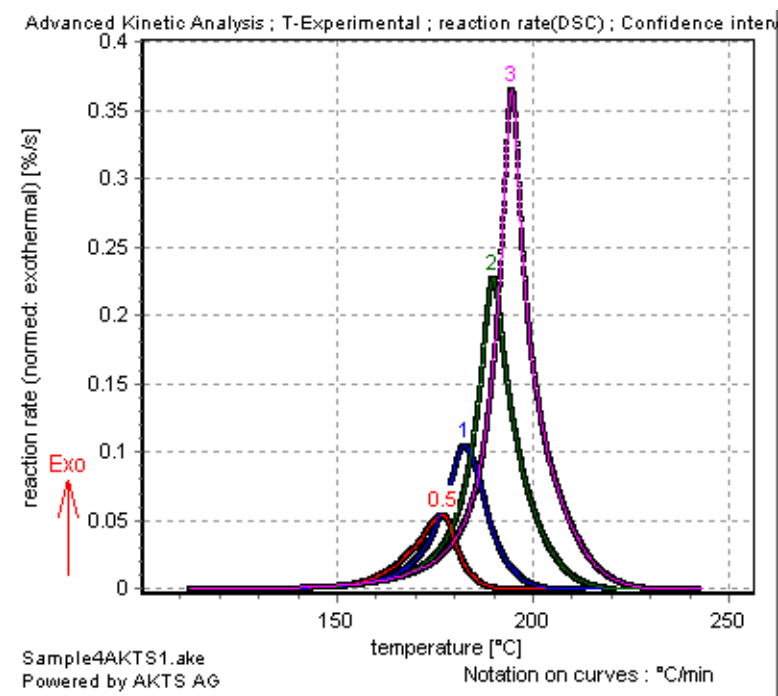

Figure 16. Comparison of measured and calculated exotherms for Sample 4 from the AKTS Thermokinetics program. Heating rates in ^{o}C/min are shown.
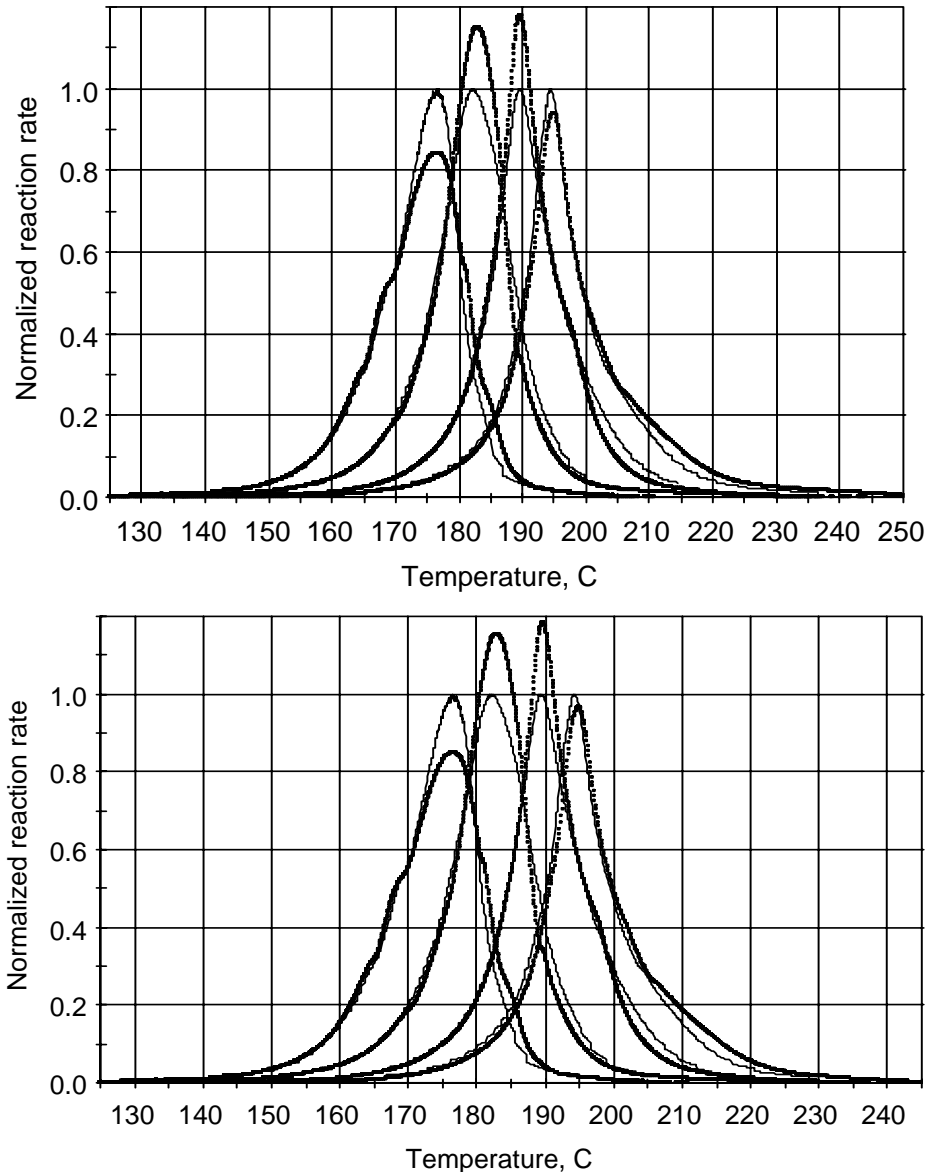
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Figure 17. Comparison of measured (points) and calculated (thin lines) reaction profiles for two baseline cuts of Sample 4 as determined by the LLNL Kinetics05 program for the isoconversional model. The top is labeled as LLNL1 and the bottom as LLNL2. The heating rates from left to right are 0.5, 1.0, 2.0, and 4.0 $^{\circ}$C/min.

As for other samples, it is interesting to compare how model fitting works compared to the isoconversional method. The first model optimized a single, extended Prout-Tompkins, nucleation-growth model against the data (second baseline cut) and is shown in Figure 18. Clearly the change in skewness with heating rate causes the model to deviate from measurement significantly. This is particularly important in that the deviation at low conversion has become quite substantial at the lowest heating rate. Of course, it is possible to get a much better fit using three parallel nucleation-growth models. Here, it is evident from both the isoconversional analyses and the data itself that

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having a higher activation energy for the middle reaction will cause it to shift less with heating rate as do the faster and slower process, thereby changing the reaction profile shape with heating rate. Results of this fit are shown in Figure 19 and Table 5, and it is much improved over a single reaction fit. The residual sum of squares has been cut approximately in half—slightly more for the fractions converted and slightly less for the reaction rates. Most important for lifetime prediction, the leading edge of reaction profile now fits extremely well.

Figure 18. Comparison of measured and calculated reaction rates for Sample 4 as determined by a fit of a single nucleation-growth reaction to the fraction converted, yielding $A=5.68\times10^{12}$ s^{-1}, $E=131.05$ kJ/mol, m=0.88, and n=1.50.
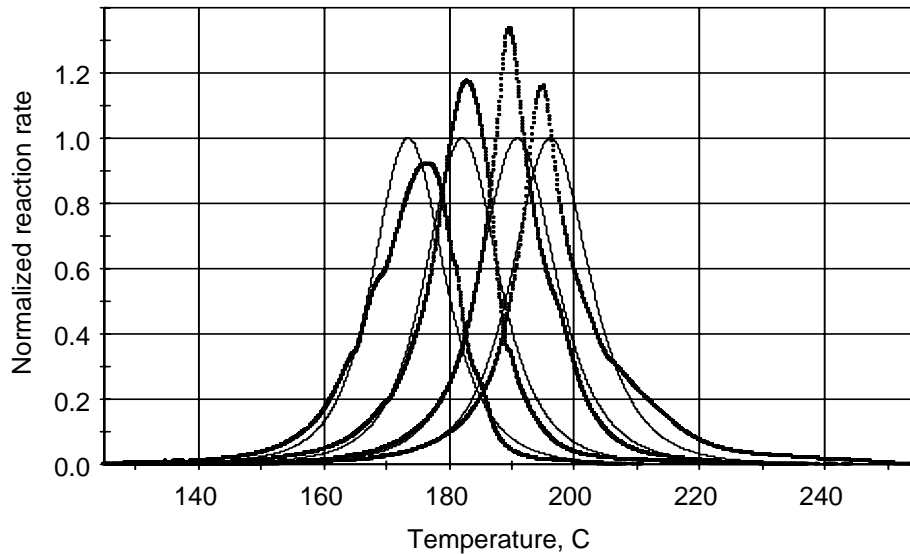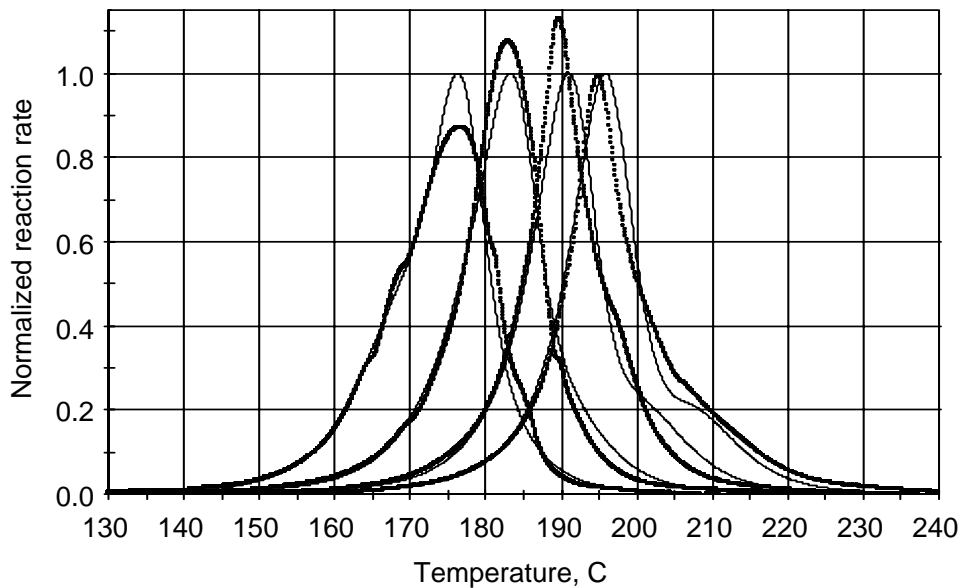

Figure 19. Comparison of measured and calculated reaction rates for Sample 4 as determined by a fit of a three parallel nucleation-growth reactions to the fraction converted. The heating rates from left to right are 0.5, 1.0, 2.0, and 4.0 $^{\circ}$C/min.

Table 5. Rate parameters for the model fit to Sample 4 data given in Figure 19.

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.238	3.79×10^9	103.63	0.82	0.76
0.493	2.43×10^{15}	153.31	0.96	1.06
0.269	6.41×10^{15}	110.49	0.93	1.38

The range of predictions for Sample 4 is also interesting, as shown in Table 6. The results from the AKTS and LLNL programs agree reasonably well with each other for all but the highest temperature. That is because the Thermokinetics program predicts final step in conversion (from about 60 to 100%) occurs between 3.7 and 3.9 years, while the same step occurs at about 2.4 and 2.8 years for the two isoconversional models from Kinetics05. This is seen more clearly in Figure 20. The faster completion of the reaction from the Kinetics05 parameters is due to their lower activation energies at high conversion, which means that the reaction rate is not slowed as much as the temperature is dropped.

What is more interesting in Figure 20 is the significant difference in prediction of the nucleation-growth models and the isoconversional models. The single nucleation-growth model is fairly easily dismissed, because it does not fit the data particularly well. However, the difference in shape of the aging curve for the 3-parallel nucleation-growth reaction model is intriguing, because it does fit the data nearly as well as the isoconversion models.

Table 6. Predictions of the five Sample 4 models for three years at the specified temperatures (^{o}C).

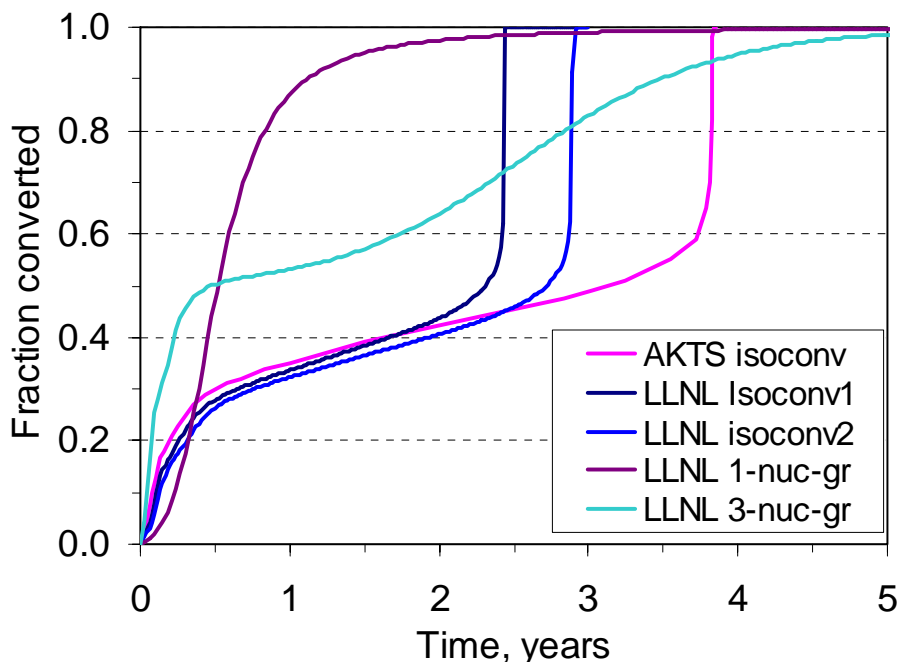| Model	25	50	80	25±10	50±30
AKTS isoconv	0.06	6.11	48.68	0.16	31.27
LLNL isoconv1	0.11	5.00	100.00	0.18	29.34
LLNL isoconv2	0.05	3.28	100.00	0.11	20.10
LLNL 1-nuc-gr	0.01	0.90	99.01	0.02	60.08
LLNL 3-nuc-gr	0.20	26.17	82.89	0.32	50.81

Figure 20. Comparison of aging predictions at 80 °C for the five Sample 4 models in Table 6.

A closer inspection reveals a phenomenon that is often overlooked—the isoconversional model actually assumes that the relative order of two processes in a complex reaction network can nearly merge but cannot cross. The isoconversional activation energy has a maximum at about 40% conversion. Likewise the activation energy of the middle reaction in the parallel nucleation-growth reaction model also has a higher activation energy. However, as the temperature is dropped, something qualitatively different is required by the two models. In the parallel model, the slowest reaction at high temperature becomes faster than the middle reaction, so the first and third reactions in that model actually cause the 50% conversion in less than 0.5 years at 80 °C. Reaction 2 then slowly occurs between 1 and 5 years. In contrast, the reactions cannot switch order in the isoconversional model, so the faster ones wait until the slower reactions are finished and then rapidly rush to completion. This is actually a more stringent limitation than in a sequential reaction, in that the middle and late reactions would occur simultaneously at the rate of the slower one in the traditional "rate-limiting-step" fashion.

This sample, therefore, provides a very interesting test of the relative validity of various reaction models, and it emphasizes the point the isoconversional method is really not model-free. It also points out the danger of assuming that, if the data can be manipulated into isoconversional form, that the predictions are necessarily valid. Not only would real aging experiments be relevant, but spectroscopic analysis of the sample might be able to determine whether the reaction components are independent concurrent reactions, sequential reactions, or something more complicated.

Sample 5

Sample 5 has similar characteristics to Sample 4, in that it is a relatively simple profile having a high temperature process that seems to separate further from the main peak as heating rate increases, and that the activation energy reaches maximum at about 40% conversion, as shown in Figure 21. However, Sample 5 does have a slight decrease in its activation energy over the initial 10%, which may or may not be real. The LLNL Kinetics05 analysis has a very substantial decrease in activation energy for the last 20% of conversion, and the Thermokinetics analysis has a rather curious dip in activation energy about 90% conversion.

Measured and calculated reactions rates are shown in Figures 22 and 23, respectively, for isoconversional analysis by the Thermokinetics and Kinetics05 programs. The AKTS profiles fit much better, but it is again clear that the complex baseline correction has altered the reaction profiles so they follow a more regular progression in change as a function of heating rate.

As for Sample 4, it is also possible to Sample 5 to a concurrent nucleation-growth reaction model. In this case, only two reactions are needed for a fairly good fit, although the high conversion part of the profile does not fit as well as for the isoconversional model. The results are shown in Figure 24 and Table 7. In this case, the model was optimized on reaction rates rather than fractions converted.
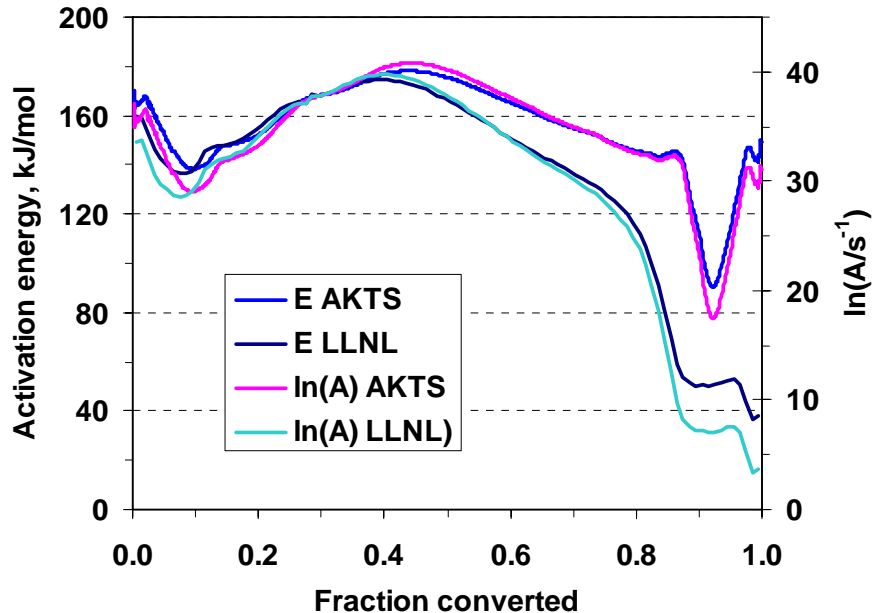

Figure 21. Conversion dependence of the activation energy and frequency factor for Sample 5 as analyzed by the AKTS Thermokinetics and LLNL Kinetics05 programs.
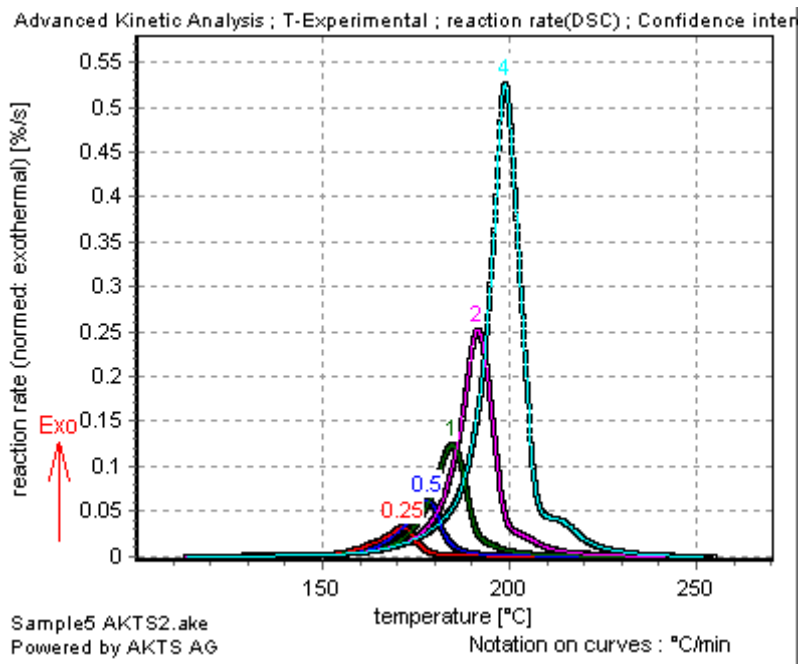
Figure 22. Comparison of measured and calculated reaction rates for Sample 5 from the Thermokinetics program.
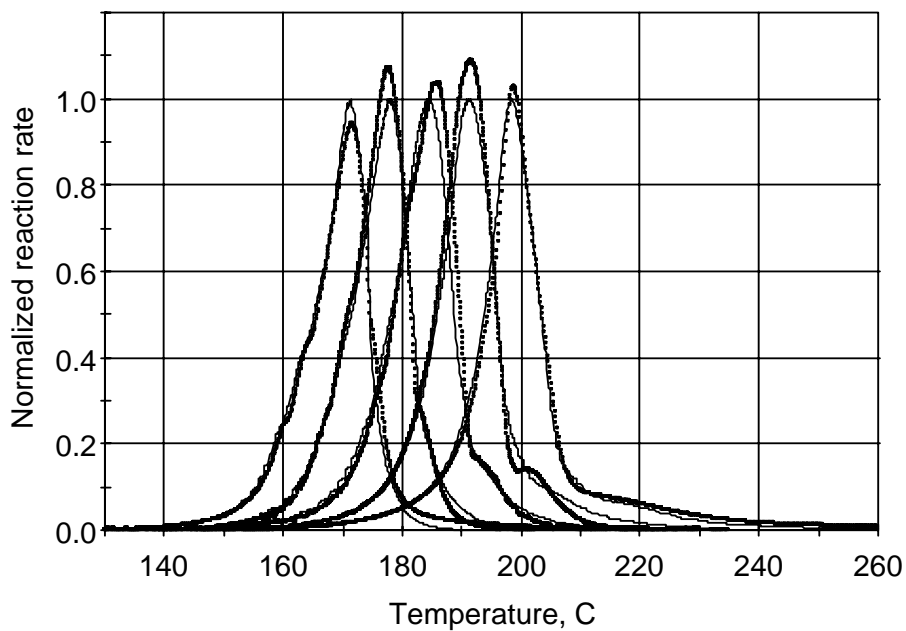

Figure 23. Comparison of measured and calculated reaction rates for Sample 5 from isoconversional analysis by the LLNL Kinetics05 program. Heating rates from left to right are 0.25, 0.5, 1, 2, and 4 °C/min.
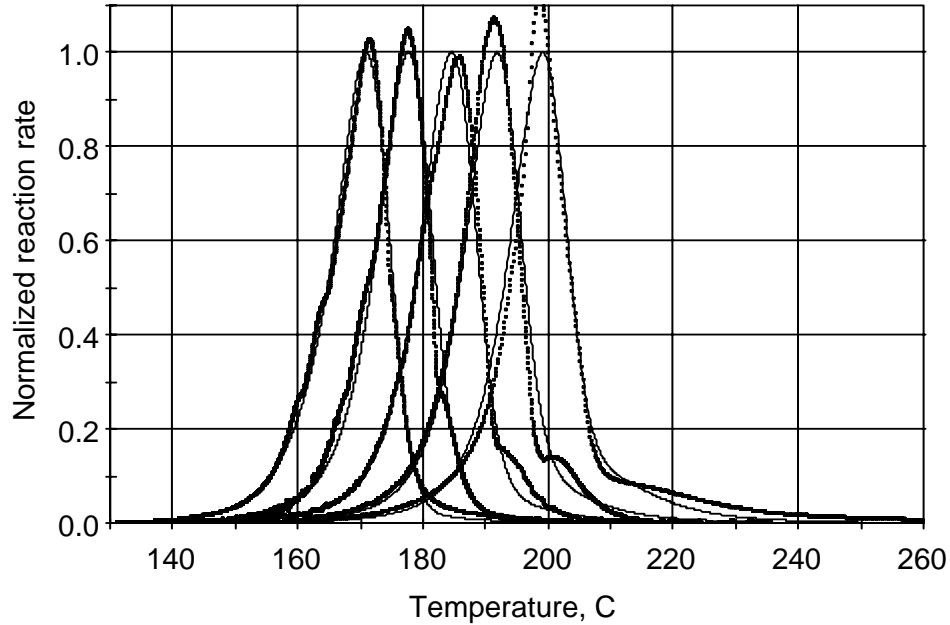
Figure 24. Comparison of measured and calculated reaction rates for Sample 5 from a fit to two parallel nucleation-growth reactions by the LLNL Kinetics05 program.

Table 7. Rate parameters for the concurrent nucleation-growth reaction model fit to Sample 5 data given in Figure 24.

Fraction	A, s^{-1}	E, kJ/mol	m	n
0.20	5.87×10^{16}	167.00	0.77	0.98
0.80	4.10×10^{9}	105.19	0.86	1.65

A summary of predictions for these three models is shown in Table 8. As for Sample 5, the slower reaction at calibration temperatures becomes the faster reaction at aging temperature for the concurrent nucleation-growth reaction, leading to enhanced aging at 50 ^{o}C, both constant and modulated. All the issues discussed for Sample 4 about whether the reaction is concurrent, sequential or some other mechanism hold here as well, and, in the absence of long-term aging studies, both additional calibration experiments at lower temperatures and spectroscopic investigation to uncover the true mechanism are warranted.

Table 8. Predictions of the three Sample 5 models for three years at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
AKTS isoconv	0.0009	0.22	37.88	0.005	14.49
LLNL isoconv	0.0004	0.06	35.84	0.001	2.26
LLNL 2-nuc-gr	0.06	10.1	27.37	0.095	20.08

Sample 6

This sample has a very noisy and complex reaction profile with very large and debatable baseline correction, so I expended very little effort attempting to derive kinetics without additional information. The AKTS isoconversional parameters and fit are shown in Figures 25 and 26. Model predictions are given in Table 9.

If one does not consider the possibility that these are phase transitions, the sample is sufficiently "reactive" that complete reaction is attained at temperatures of 50 ^{o}C and above. However, such an extremely high activation energy for a reaction that occurs at such a low temperature suggests that this is a thermodynamically inhibited process of some type—either a dehydration inhibited by water vapor or a phase transition. In this case, proper kinetic analysis would include the thermodynamic inhibition term, $1-1/K_{eq}$, along with whatever kinetic rate law is appropriate. The Kinetics05 program has the capability of fitting such a model,[9] but additional information about the sample and conditions are required.

If this is a phase transition, the proper prediction of fraction converted at 25% may be zero, and the proper prediction of fraction converted at 50 ^{o}C may be close to 50%. About the only certain prediction is that sample should be completely converted at 80 ^{o}C.
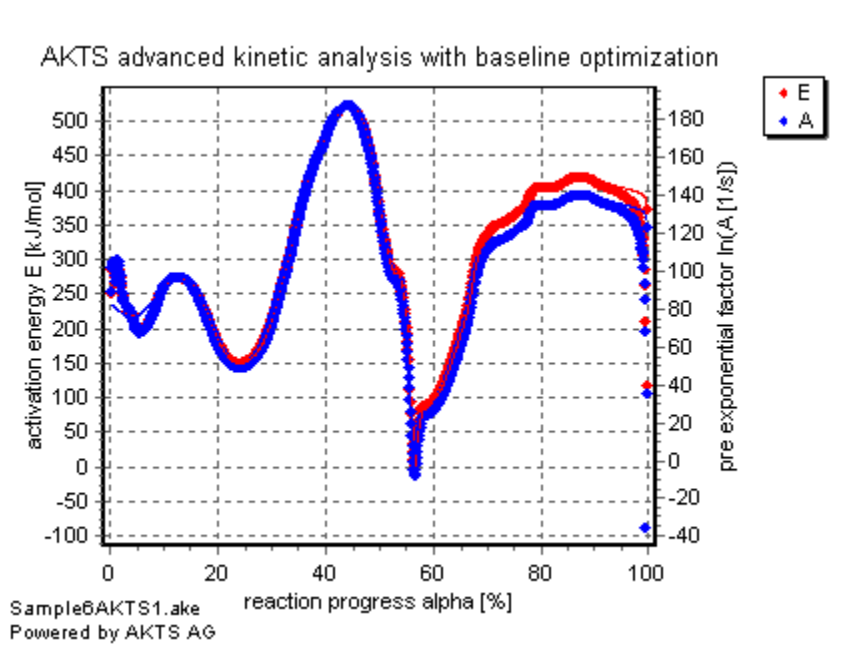

Figure 25. Activation energy and frequency factor as a function of conversion for Sample 6.
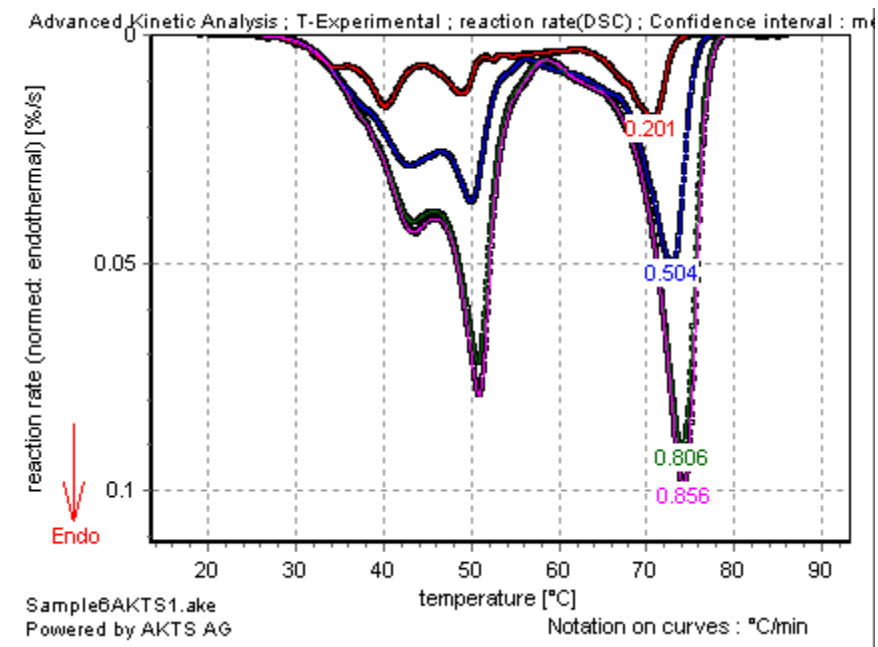
Figure 26. Comparison of measured and calculated reaction rates for Sample 6. Heating rates are 0.20, 0.50, 0.81, and 0.86 ^{o}C/min.

Table 9. Predictions of the AKTS isoconversional model for three years at the specified temperatures (^{o}C). The predictions are highly suspect, however, since this is likely a thermodynamically inhibited process.

Model	25	50	80	25±10	50±30
AKTS isoconv	40.5	100	100	69.5	100

Sample W1

TGA rather than DSC data is provided for Sample W1. This sample is listed as an energetic material, and Figure 27 shows clear evidence for a thermal explosion at about 200 ^{o}C for heating rates of 5 ^{o}C/min and faster, which is presumably because the heat generated by decomposition cannot be dissipated fast enough to prevent thermal runaway.
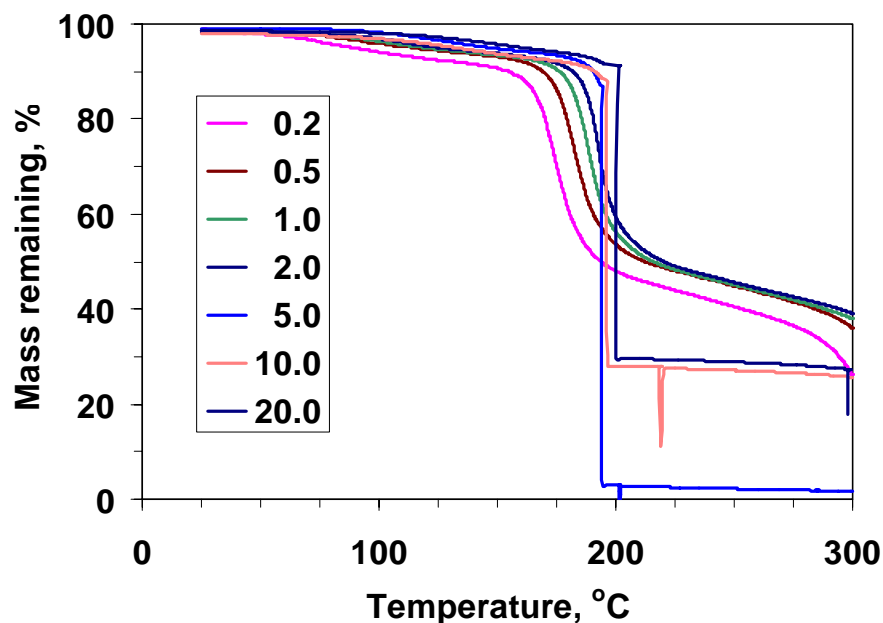

Figure 27. Remaining mass as a function of temperature for energetic material Sample W1. Thermal explosion occurs at 5 ^{o}C/min and higher rates.

Another issue with this sample is that both the thermal histories and the reaction data oscillate. An expanded view of fraction-reacted versus temperature for the lowest four heating rates is shown in Figure 28. The fact that the mass goes up and down is a significant limitation to any chemical reaction kinetics derived therefrom. Figure 29 shows the oscillations in reaction rate and in the difference between sample and reference temperatures. There apparently is a lag time between temperature measurement and the mass oscillations, which further compromises the kinetic analysis. Furthermore, it appears that the lowest heating rate data may have some drift, leading to an overestimation of conversion. My first suggestion for this material would be to collect data on a more stable instrument if one wants good kinetics.
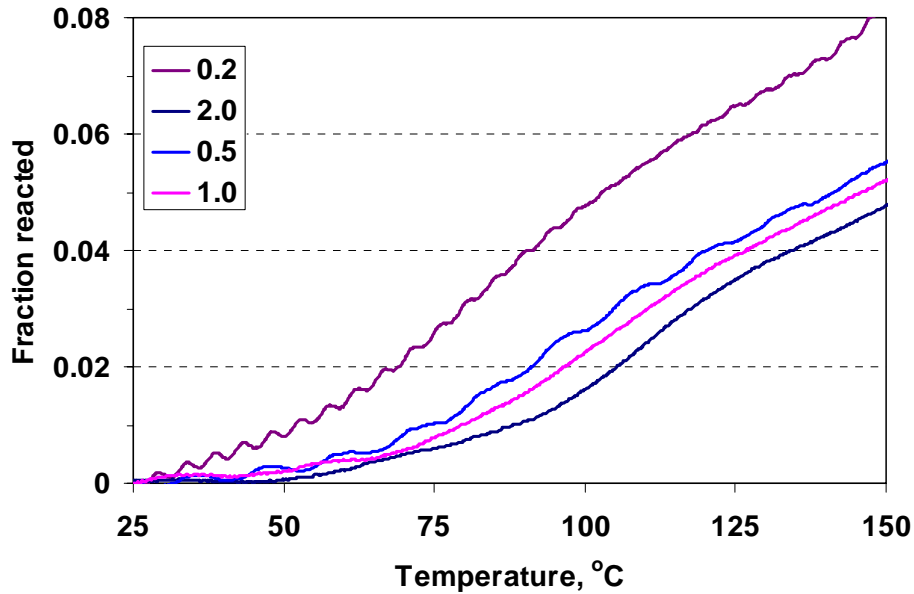
Figure 28. Oscillations in the mass fraction converted for Sample W1, using the highest observed mass as zero reaction. These oscillations compromise the kinetic analysis at low conversions.
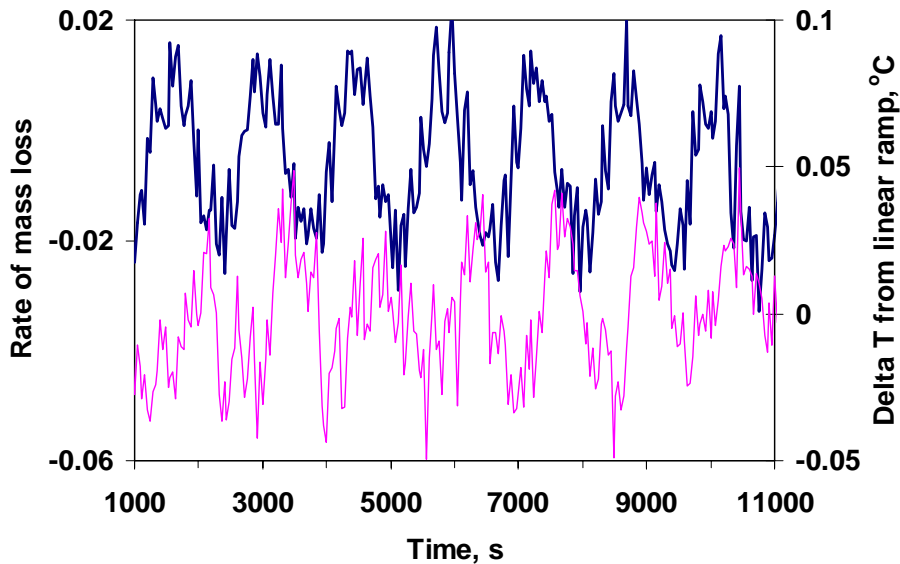
Figure 29. Oscillations in the nominal sample temperature and rate of mass loss. The displacement between the oscillations further compromises the kinetic analysis.

The fact that the mass does not go to zero means that one needs to chose a criterion for conversion. The AKTS Thermokinetics version we have automatically scales the last data point in each file to 100% completion, which makes no sense in this case. Kinetics05 allows the user to choose a completion criterion, and I chose 100% mass loss.

For the isoconversional model, Kinetics05 calculates A and E only up to the lowest conversion in any file. A and E could be calculated up to the second-highest conversion, but then the number of experiments used above the lowest conversion would vary with conversion, which might cause spurious effects. Consequently, I did not use the data at heating rates of 5.0 °C/min and higher. The resulting A-E dependences upon conversion are shown in Figure 30, and a comparison of measured and calculated fractions reacted is shown in Figure 31.

The activation energy and frequency factor rapidly rise after the first 5% of the mass loss. This characterizes the slow loss over roughly the 50-150 °C/range, and the parameters have considerable uncertainty due to possible small errors in the initial mass. The energy is roughly constant at 260 kJ/mol from 10 to 35% conversion. At that point, both A and E drop quickly to a minimum at about 50% conversion.

The calculated and measured fractions reacted agree very well for the lowest three heating rates, but at 2 °C/min, the fraction calculated initially lags and then quickly changes at 200 °C. As for samples B3 and 4, this may be indicative of an autocatalytic runaway caused by the domed activation energy profile, which then leads to a thermal runaway at slightly faster heating rates when the heat cannot be dissipated fast enough.
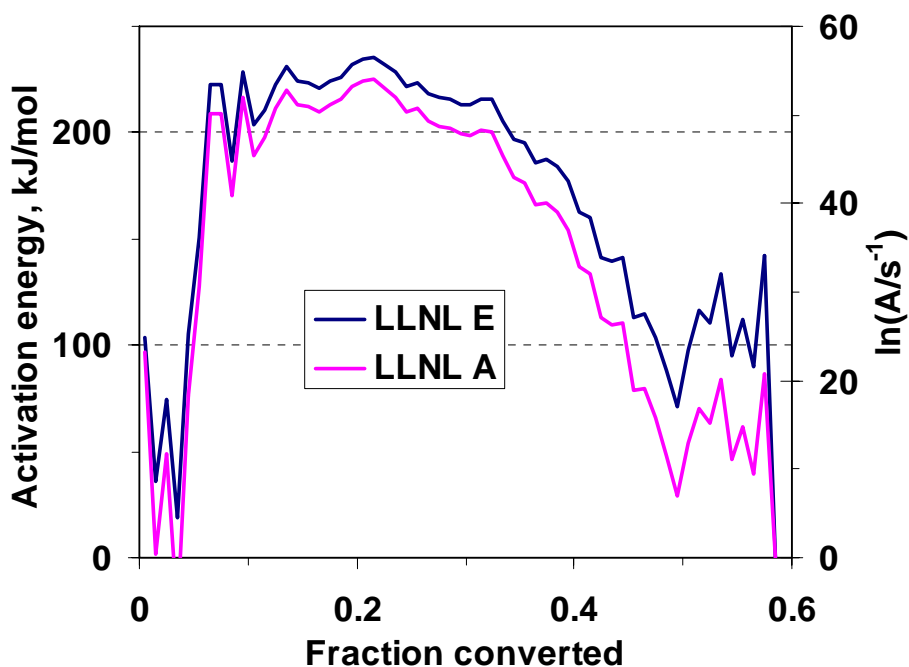

Figure 30. Isoconversional kinetic parameters for energetic material Sample W1 derived from LLNL Kinetics05.
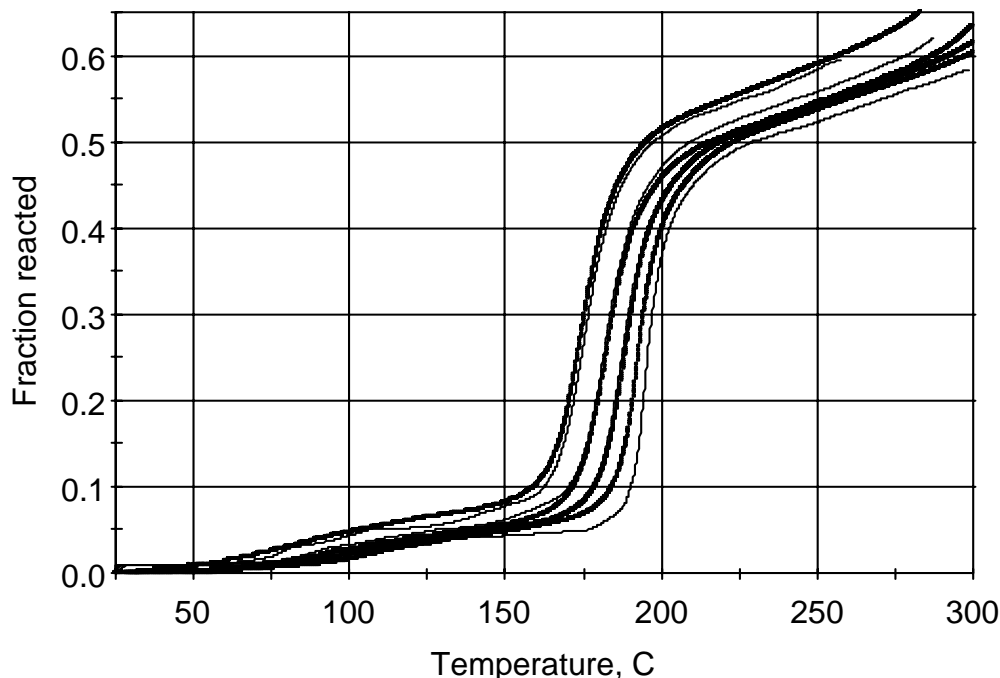
Figure 31. Comparison of measured and calculated fractional mass loss at heating rates of 0.2, 0.5, 1.0, and 2.0 °C/min (from left to right) for energetic material Sample W1 derived from Kinetics05.

It is also possible in principle to fit chemical reaction models to the Sample W1 data, but the models available in Kinetics05 are insufficient to work very well past mid-conversion. One fit to the first two reaction components is shown in Figure 31. The first reaction accounts for 7% of the reaction and has manually optimized reaction parameters of $A=5\times10^8$ s^{-1}, $E=83.7$ kJ/mol, and n=2.5, while the second reaction accounts for 45% of the mass loss and has regression-optimized reaction parameters of $A=1.2\times10^{20}$ s^{-1}, $E=198.7$ kJ/mol, m=0.50, and n=2.05. These parameters are qualitatively similar to the isoconversional parameters shown in Figure 30. They may be able to predict aging at low conversions (<40%) fairly well, but they will clearly fail at higher levels of aging. Predictions of aging are given for the ICTAC conditions in Table 10, and the isoconversional and parallel reaction models are, in fact, similar.

Table 10. Predictions of the two Sample W1 models for three years at the specified temperatures (°C).

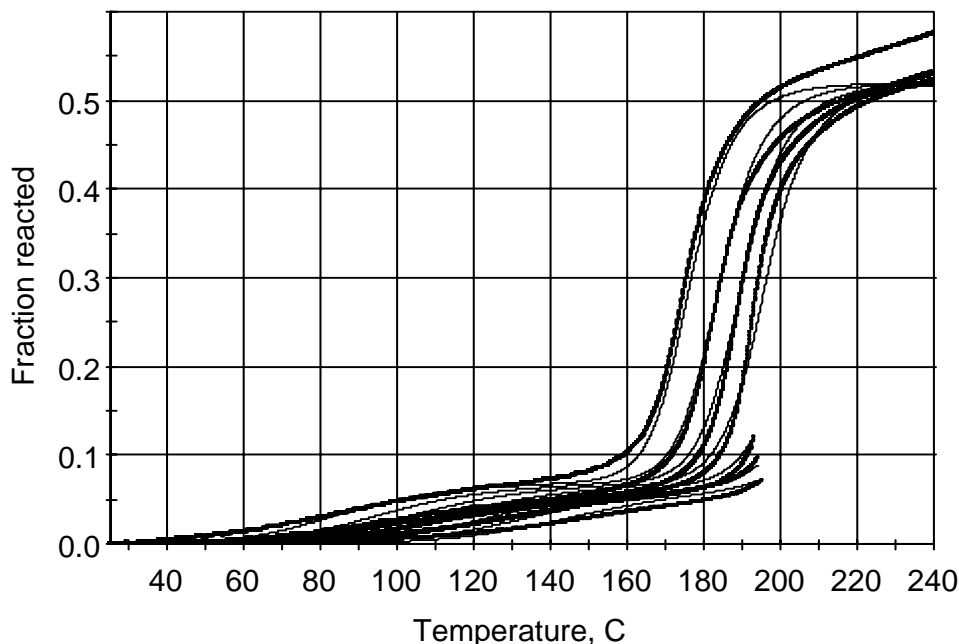| Model	25	50	80	25±10	50±30
LLNL isoconv	4.32	5.07	6.06	4.49	6.00
LLNL 2-rxn	6.76	6.96	9.00	6.80	7.01

Figure 31. Approximate fit of the first two reaction components in Sample W1 to parallel nth-order and nucleation-growth reactions. The additional three data sets, truncated before thermal runaway, are at 5, 10, and 20 $^{\circ}$C/min.

Sample W2

TGA data is also provided for polymeric sample W2. The primary decomposition of this sample starts in the 300 $^{\circ}$C range for the slowest heating rate, so for typical pyrolysis activation energies, the primary decomposition reaction is irrelevant for lifetimes at 80 $^{\circ}$C except for many years. Only the feet of the pyrolysis curves influence kinetics relevant to the aging predictions of the ICTAC study. Ironically, the data at the slowest heating rate is qualitatively different from all the other data sets. Consequently, it indicates either a change in mechanism, e.g., from a pyrolysis-dominated to oxidation-dominated mechanism, or it indicates instrumental instability over the long time of the experiment. Experimental work, not kinetic analysis, is the proper way to distinguish between these two alternatives. Consequently, the kinetic analysis presented here really addresses "if-then" possibilities.

The first step is to look at the low conversion data in more detail. For 0.5 to 20 $^{\circ}$C/min, one can see that the fraction-converted lines cross each other, violating the isoconversional principle. One could adjust in initial fraction reacted to that they follow a logical progression, but one still needs to estimate the magnitude of the initial displacement. It would be best to do so iteratively, but that must be done manually in Kinetics05. The AKTS thermokinetics code may be able to do this with its baseline optimization feature, but since it works in the differential mode and the initial experimental rate is not zero, it would appear that their method is not appropriate.
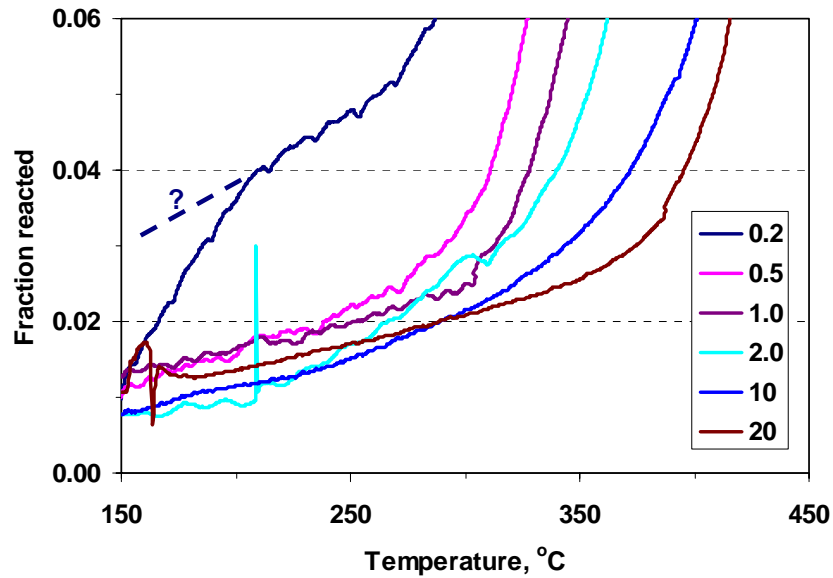
Figure 32. Fractional mass loss from polymeric sample W2, showing the internal inconsistency in the data at low mass loss.

The next issue is that the data at 0.2 °C/min are qualitatively different than for the other experiments, except that fastest heating rate followed the same mass vs. time trajectory until a discontinuous break to a slower rate of mass loss. Another problem with the lowest-rate data is that the high-temperature tail is different. One might presume that the glitch at 480 °C marks the end of the reliable data, but that, of course, is an assumption. The other possibility is that direct oxidation has become relatively more important due to the longer time scale.

Figure 33. Inconsistency of the asymptotic mass loss at 0.2 °C/min compared to the other heating rates.

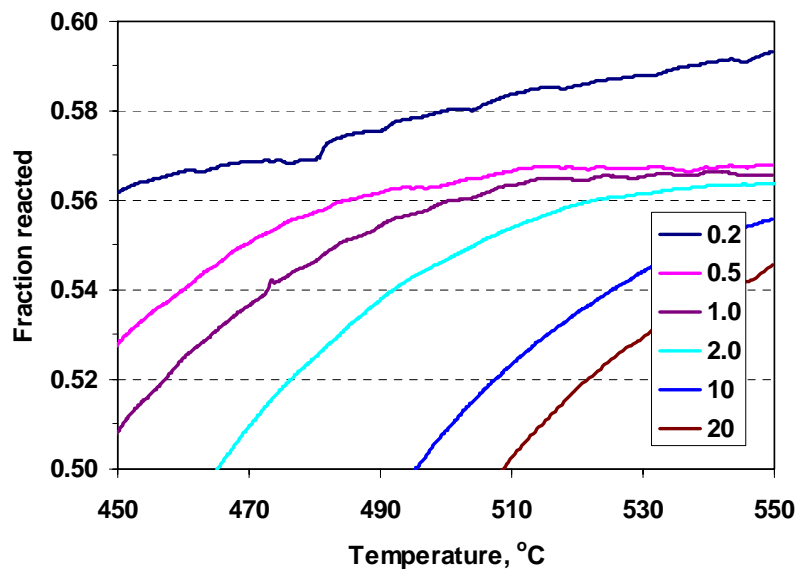Another issue is that no reliable conversion estimates can be made at fractions reacted lower than reported in the experiments. In this case, any mass loss prediction for fractional mass loss less than 1% is meaningless. There could have been, for example, a discontinuous mass loss near 100% due to a drying process. Furthermore, the lack of thermal history prior to the first recorded mass loss is an issue, since integration over that thermal history is required for accurate kinetic analysis.

The bottom line is that this data set is really not adequate for the stated ICTAC objective of testing aging predictions at low temperatures and conversions. However, with these limitations as background, an attempt was made to derive plausible kinetics from these data by adjusting the initial mass loss so that it followed a more regular trend and by deleting the high and low temperature data at 0.2 $^{\circ}$C/min. Also, all thermal histories were extrapolated back to 110 $^{\circ}$C.

The results of the isoconversional kinetic analysis from Kinetics05 are given in Figure 34. The activation energy and frequency factor start low and quickly reach an approximately constant level for the remainder of the mass loss.   The corresponding comparison of measured and calculated fractions reacted is shown in Figure 35.
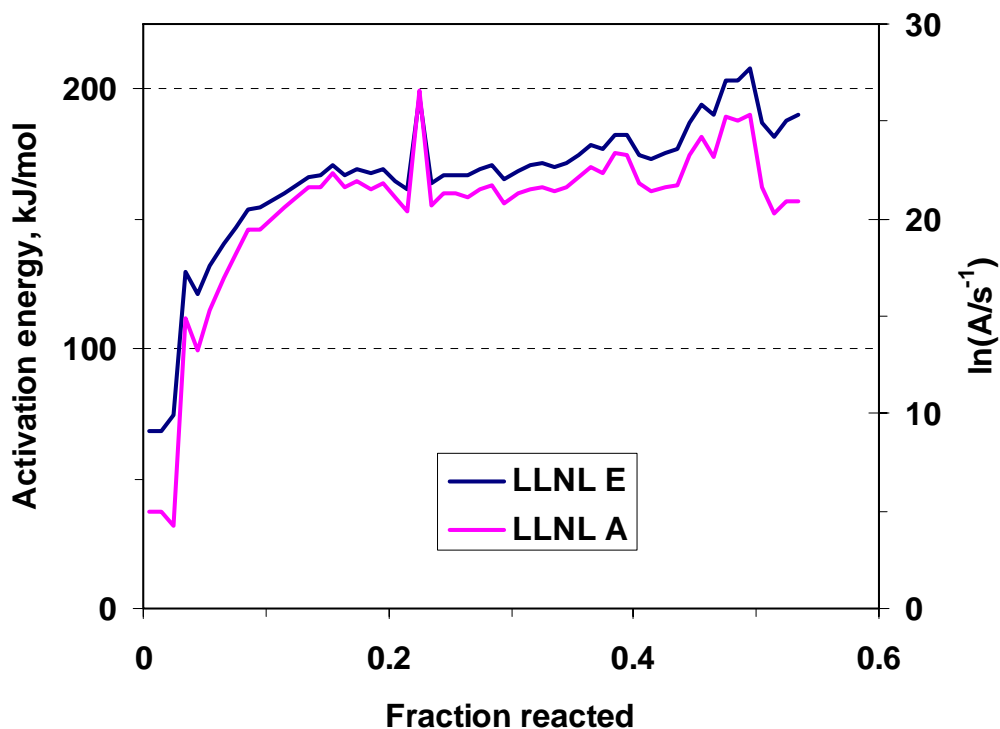

Figure 34. Isoconversional parameters from Kinetics05 for polymeric sample W2.
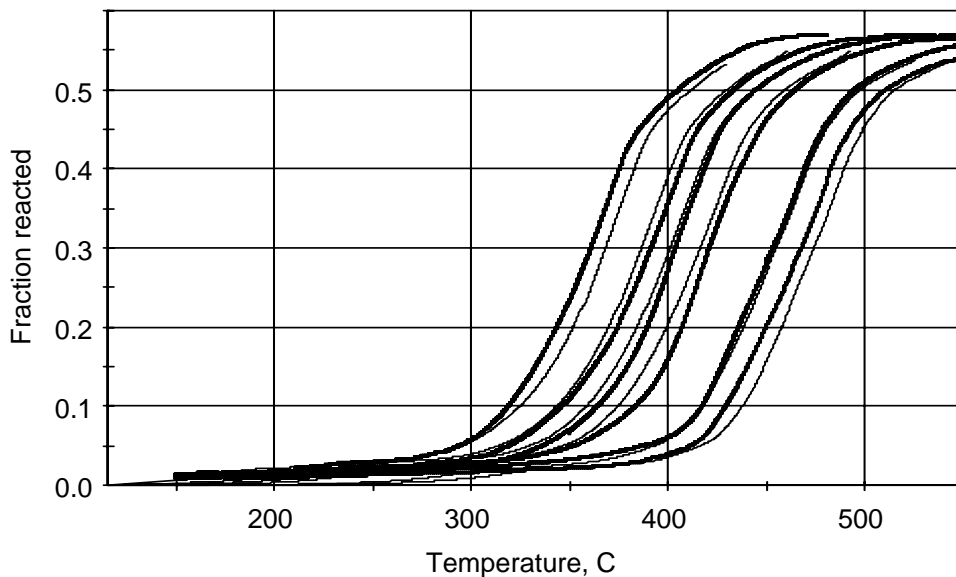
Figure 35. Comparison of measured and calculated fractional mass loss for Sample W2 for the isoconversional kinetic parameters derived by Kinetics05. Heating rates from left to rigt are 0.2, 0.5, 1, 2, 10, and 20 °C/min.

Sample W2 data were also fitted to two parallel nth-order, Gaussian-activation-energy-distribution reactions, and measured and calculated fractional mass loss is given in Figure 36. The reaction parameters are given in Table 11. The fit is not quite as good. The aging predictions of both the isoconversional and nth-order Gaussian model are given in Table12. The isoconversional predictions are slightly larger, which might be expected due to the better fit for the 3-7% conversion level at the slowest heating rate.

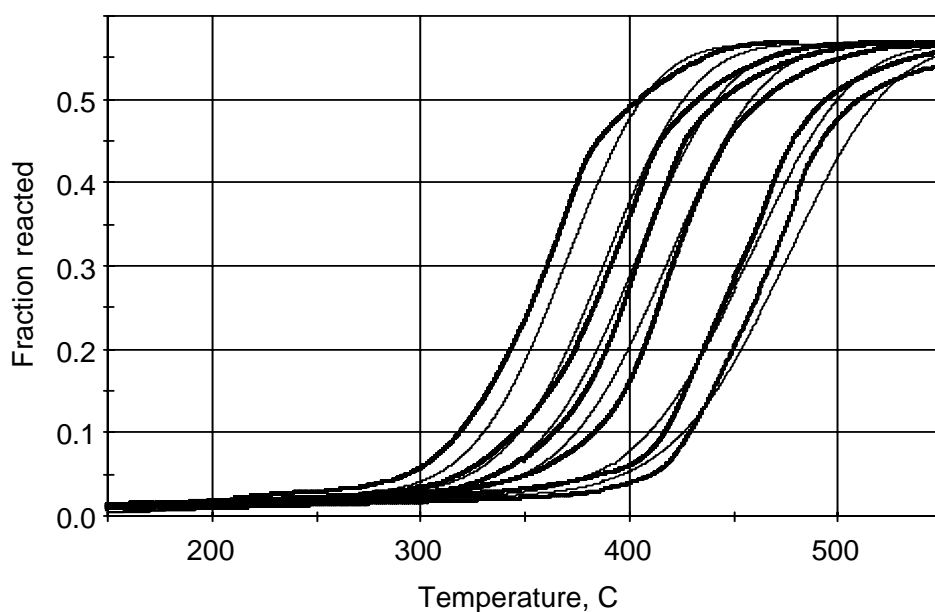**Figure 36.** Comparison of measured and calculated fractional mass loss for the concurrent nth-order Gaussian model derived for Sample W2 using Kinetics05.

Table 11. Rate parameters for the concurrent nth-order Gaussian reaction model fit to Sample W2 data given in Figure 24.

Fraction	A, s^{-1}	E, kJ/mol	σ, % of E	n
0.025	4.07×10^{6}	83.86	16.15	1.45
0.542	2.60×10^{9}	161.59	1.00	2.00

Table 12. Predictions of the two Sample W2 models for three years at the specified temperatures (^{o}C).

Model	25	50	80	25±10	50±30
LLNL isoconv	1.53	3.46	4.00	1.84	4.00
LLNL 2-rxn	1.27	1.74	2.17	1.31	1.97

Discussion

The first requirement for good kinetic parameters is good kinetic data. Data processing can overcome only a limited amount of spurious data and noise, and after that, the results become highly dependent on the assumptions used to preprocess the data prior to formal kinetic analysis. Examples are baseline selection, including the functional form for nonlinear corrections, which is particularly important for DSC data, and elimination of mass drift for long TGA experiments. Larger sample sizes should be used at lower heating rates to increase signal-to-noise and signal-to-baseline resolution. The temperature and mass oscillations in Sample W1 is another good example of a characteristic to be avoided.

Data should be collected at the earliest possible point in the reaction (either rate or fraction reacted), and the thermal history should be measured and included prior to that point if the rate or fraction reacted is not truly negligible. Sample W2 is a good example of a case where the low-temperature data is improperly trimmed, which leads to significant limitations in the calibration of any kinetic model in the mass loss region overlapping that for which predictions are desired.

A minimum prerequisite for reliable predictions of a kinetic model is that it visually fits the data well over a wide range of thermal histories. The AKTS Thermokinetics program is a bit misleading in that regard, since the comparison between measurement and calculation includes a sometimes-significant adjustment of the data via a complex baseline correction so that it conforms to the isoconversional assumption. To the extent that the reaction truly does follow the isoconversional assumption, this optimization process can lead to better isoconversional parameters, but this is not immediately obvious from the plots shown by AKTS. Also, the AKTS baseline optimization process appears to sometimes eliminate real signal, which is what I expect causes the lower predictions at low temperature for Sample 1.

A good visual fit to a model is not a guarantee that it will extrapolate reliably outside the range of calibration. For Sample 1 (simulated data) and for Sample 2, the predictions of isoconversional and parallel reaction models are quite similar. Likewise, the LLNL isoconversional and parallel reaction models give similar predictions for conversions less than 35% for Sample B3. However, there are significant differences between LLNL and AKTS isoconversional models for that same sample that can be related to the baseline correction. To the extent that the assumptions imbedded in the AKTS baseline optimization are valid, along with the isoconversional assumption itself, the predictions using the AKTS Thermokinetics program may be more accurate in this case.

In contrast, the isoconversional and parallel model predictions are significantly different for Samples 4 and 6. The reason is that the parallel reactions cross in relative reactivity over the extrapolated temperature. The second reaction at calibration temperatures has an activation energy 43 kJ/mol higher than the third reaction, so it quenches more rapidly and becomes slower at low temperatures. Although not always realized, and sometimes obscured by the "model-free" nomenclature, the isoconversional model contains a sequential reaction assumption. Even though the reaction rate may be intrinsically faster in the later stages of reaction, that portion cannot start until the earlier, slower reactions are completed. This leads to a chemical kinetic runaway after an induction time, as shown in Figures 14 and 20. This sequential reaction assumption implicit in the isoconversional model may be the correct one for energetic materials. For example, if a stabilizer is consumed during the first portion of the reaction, the average activation energy may decrease and the overall reaction rate may increase as the propagation chain length becomes longer. The apparent activation energy is a weighted average of initiation and propagation activation energies, and initiation reactions typically have higher activation energies.

If the sequential reaction character of the isoconversional model is the central characteristic that leads to a proper prediction of isothermal induction times, that characteristic should not be obscured by statements that its better predictions compared to primitive model fitting are because it fits the calibration data better. Even though AKTS Thermokinetics and some other kinetic fitting programs are quite limited in the types of models they can fit, and therefore cannot match experimental data very well using that approach, other programs such as Kinetics05, the Netzsch Thermokinetics program,[10] and the CISP kinetics program[11] can match complex reaction profiles by model fitting with multiple reactions. Instead, the essential point is to understand is that some reaction networks are dominated by sequential reaction characteristics and that a good fit to a parallel reaction model does not assure reliable extrapolation.

Likewise, good fits by the isoconversional approach do not assure good extrapolations outside the calibration range if the isoconversional assumption is not completely valid. As an example, I constructed a simulated data set using the following chemical reaction network, which has both parallel and sequential characteristics. In fact, the way the reaction profiles change as a function of heating rate were inspired by some of the data sets in this exercise:

Table 13. Reaction parameters used to derive a second set of simulated data

Reaction	A, s^{-1}	E, kJ/mol	σ, % of E	n
X→Y	1.00×10^{15}	159.0	5.00	2.00
X→Z	1.00×10^{12}	125.5	0.00	1.00
Y→Z	4.00×10^{15}	159.0	0.00	2.00

The resulting data was subjected to isoconversional analysis by the AKTS Thermokinetics and LLNL Kinetics05 programs and fitted to two parallel nucleation-growth models using Kinetics05. The resulting fits from Kinetics05 are shown in Figure 37. Both fits are very good, and the isoconversional fit is slightly better. The two activation energies from the parallel nucleation-growth model are 146.6 and 147.4 kJ/mol, and the isoconversional activation energy varied between 140 and 160 kJ/mol. Regardless of the quality of the fits, both approaches failed to accurately predict the amount of conversion for the ICTAC aging conditions, as shown in Table 14. The AKTS code again subtracted too much baseline and underpredicts the initial reaction. The results are mixed in the intermediate temperature region, but all models overpredict conversion at 80 ^{o}C.

Table 14. Predictions of the three models fitted to LLNL simulated data for three years at the specified aging temperatures (^{o}C).

Model	25	50	80	25±10	50±30
AKTS isoconv	0.0009	2.24	63.1	0.008	7.78
LLNL isoconv	0.06	2.82	65.76	0.12	12.99
LLNL 2-nuc-gr	0.04	3.17	74.86	0.09	21.25
Ground Truth	0.11	2.58	53.5	0.2	15.24

The essential point here is that a good fit does not by itself assure accurate extrapolations. The essential characteristics of the reaction network have to be properly represented by the model, and I here explicitly consider the isoconversional approach a model. The isoconversional approach is quite flexible and easy to use to fit to complex reaction profiles. Furthermore, it appears usually to work well. Consequently, its place in modern kinetic analysis is well deserved. That said, it should always be remembered that its assumptions may not hold for some cases. Fitting of complex reaction networks is generally more time consuming, and the resulting models are usually more reliable if supplemental information about the reaction characteristics is available. They are better suited to situations where it is important to keep track of sources and sinks, and they have a particular advantage when both endothermic and exothermic reactions are present.
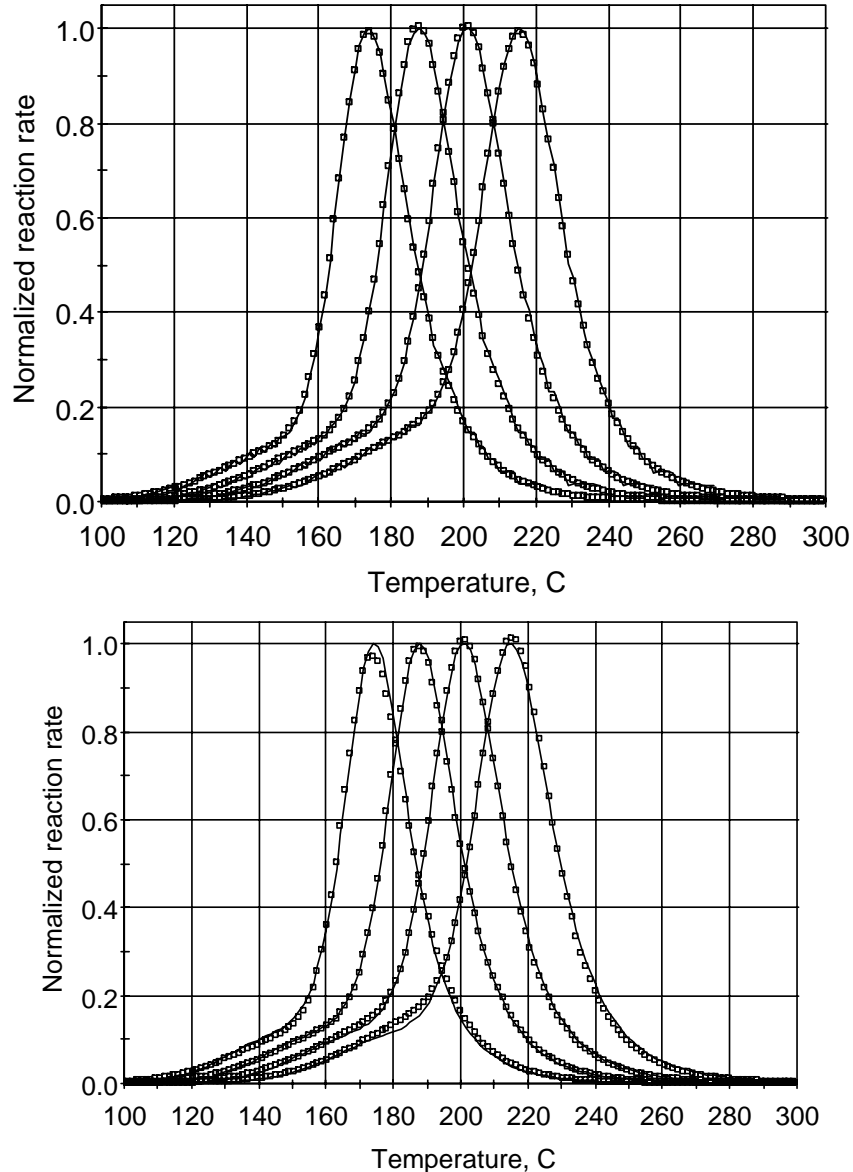
Figure 37. Comparison of measured and calculated reaction rates for the isoconversional (top) and parallel nucleation-growth reaction models derived using Kinetics05.

Although the current exercise included only constant-heating-rate experiments, a combination of constant-heating-rate and isothermal experiments better exposes the reaction network characteristics and more thoroughly constrains the kinetic model. This is particularly true for sequential and autocatalytic reactions, where induction and acceleratory phases are important, and it becomes even more important when multiple processes are evident in the constant-heating-rate profile.

Another factor not considered here is the effect of gas environment on the decomposition of a solid. Some autocatalytic behavior is enhanced in a closed container, in which the product gases can further react with the starting material. The degree of reaction may be

enhanced by minimizing the void volume of the container. The behavior is common for energetic materials, of which the ICTAC sample set contains several. Other reactions are self-inhibiting, such as dehydration and decarbonation reactions. If the products are not effective removed, the reaction slows and can even stop if an equilibrium partial pressure is attained. Sample 6 has signs of thermodynamic inhibition, but not enough is know about the reaction to understand the nature of the inhibition and what type of model would be correct. Sample 6 could just as easily be a phase transition for which gas generation is not even involved. This example shows the folly of deriving kinetic parameters for unknown reactions in undefined conditions.

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