

Predicting the Shelf Life of Energetic Materials via Kinetic Analysis of Decomposition Data Gathered by Using Thermal Analysis Techniques

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The shelf life of energetic materials (EMs) (i.e., explosives, propellants, and pyrotechnics) is strictly linked to safety and functionality. Therefore, a priori knowledge of this parameter is of paramount importance. The standard method for predicting the shelf life of EMs, the so called multi temperature aging method, is tremendously time and money consuming. Specifically, it consists of massive isothermal accelerated aging tests at temperatures typically between 40 and 80°C for relatively long time periods (from months to years) with different aging time intervals, followed by analysis of the aging-induced changes. A subsequent kinetic analysis with Arrhenius evaluation provides the effective activation energy for calculating shelf life at lower storage temperatures. In this work, a much less time- and resource-intensive approach is presented as a possible alternative for the shelf life prediction of EMs. This approach is based on the kinetic analysis of decomposition data gathered by using thermal analysis techniques, which are usually operated under dynamic (i.e., non-isothermal) conditions and possess the advantage of a rapid reaction process, and requires accelerated aging tests only to validate the kinetics extracted from such data. Results from the literature to support this alternative approach are discussed, with particular emphasis on those obtained by the present authors.

1. Introduction

Energetic materials (EMs) (i.e., explosives, propellants, and pyrotechnics) can quickly react to release a huge amount of energy and gas, even in the absence of oxygen. This feature makes them attractive for both military and civilian applications. Unfortunately, EMs are thermodynamically unstable substances – their existence is only due to kinetic reasons. For most of these materials, slow chemical decomposition already occurs at room temperature and even more so at elevated temperatures (as in the case of exposition to fires). As a rule of thumb, EMs with an activation energy of decomposition higher than 170 kJ mol⁻¹ are stable for thousands of years at room temperature, whereas EMs with an activation energy of decomposition lower than 155 kJ mol⁻¹ have limited thermal stability (Manelis et al., 2003). Table 1 quantifies the activation energy of decomposition for different classes of organic EMs. As can be seen from this table, aromatic and aliphatic nitro compounds, secondary nitramines, and organic azides are relatively stable, whereas aliphatic nitrate esters suffer from much lower stability.

The occurrence of decomposition causes the aging of EMs with the consequent compromise of storage and handling safety as well as of functionality. Therefore, a priori knowledge of the shelf life of EMs, i.e., the time interval during which they can be stored, handled, and used without any danger, is of paramount importance. In order to reduce the time scale for aging studies, which are relevant regarding assessing the safe and reliable use of EMs, accelerated aging tests (i.e., artificial aging tests at temperatures higher than ambient temperature) are generally used. Among the stability test methods based on accelerated aging, the multi temperature aging method is the only method that allows for predicting shelf life (Vogelsanger, 2004). Specifically, this method consists of massive isothermal accelerated aging tests at temperatures typically between 40 and 80°C for relatively long time periods (from months to years) with different aging time intervals, followed by analysis of the aging-induced changes. A subsequent kinetic analysis with Arrhenius evaluation provides the effective

activation energy for calculating shelf life at lower storage temperatures. An example of the practical application of this approach to a nitrocellulose-based propellant can be found in NATO-AOP 48 Ed. 2 (2008). The accelerated aging process of the propellant was tracked using measurements of the content of the stabilizer performed by high performance liquid chromatography (HPLC) analysis. The content of the stabilizer was measured after accelerated aging for up to 6, 23, and 91 days at 80, 70, and 60°C, respectively. The kinetic evaluation gave the best fit for reaction order $n = 0.58$. The obtained activation energy value ($135.3 \text{ kJ mol}^{-1}$) allowed reliable extrapolation to lower temperatures. Thus, a shelf life of 41 years at 25°C was calculated, with the failure criterion defined as a 50% decrease in the content of the stabilizer.

Table 1: Activation energy of decomposition for different classes of organic EMs.

Class of Organic EMs	Activation Energy of Decomposition (kJ mol^{-1})*
Aromatic nitro compounds	190–290
Aliphatic nitro compounds	230–260
Secondary nitramines	170–200
Organic azides	165–170
Aliphatic nitrate esters	155–190

* Values taken from Vogelsanger (2004)

The multi temperature aging method suffers from some important limitations, including its difficult application to non-isothermal aging (Dubois and Perreault, 2002). Furthermore, it is tremendously time and money consuming. More effective approaches for predicting the shelf life of EMs are therefore necessary.

Different thermal analysis techniques, such as thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), have been widely used to investigate the decomposition of EMs, even as simultaneous techniques (i.e., TG/DTA and TG/DSC) and in combination with mass spectrometry (MS) and/or Fourier-transform infrared spectroscopy (FTIR) (these latter for identifying the reaction products) (Benhameda and Trache, 2020; Liu, 2021; EL-Sayed, 2022). These techniques are usually operated under dynamic (i.e., non-isothermal) conditions and possess the advantage of a rapid reaction process. The kinetics of the thermal decomposition of EMs can be extracted from thermal analysis data and, once their reliability for extrapolation outside the range of calibration has been thoroughly assessed, used to predict the shelf life – to this end, the failure threshold needs to be defined as a function of the limiting extent of conversion. In this work, this much less time- and resource-intensive approach is presented as a possible alternative for the shelf life prediction of EMs. Results from the literature to support this alternative approach are discussed, with particular emphasis on those obtained by the present authors.

2. Results from the Literature

Results to support the perspective outlined in this work come from few literature studies (Li and Cheng, 2010; Kim et al., 2018; Harter et al., 2022; Sanchirico et al., 2022a). In such studies, both isoconversional (Kim et al., 2018; Harter et al., 2022) and model-based (Li and Cheng, 2010; Sanchirico et al., 2022a) methods were adopted to determine the decomposition kinetics of energetic materials (EMs) from the data of thermal analysis experiments performed under dynamic conditions at different heating rates. In the latter methods, the kinetic law is predetermined based on the thermal behavior of the substance under examination. This predetermination is not needed with the former methods. However, the isoconversional methods, also known as “model-free” kinetic analyses, are not assumption-free methods. The validation of the kinetics obtained from data gathered by using thermal analysis techniques, i.e., the assessment of their reliability for extrapolation outside the range of calibration, is a key step, especially when they are intended to predict a very slow decomposition phenomenon such as the aging process. In this case, experimental aging data (i.e., low temperature, long term decomposition data) are needed. In all the above cited studies, kinetic predictions were compared with experimental data obtained on actual aged samples.

Kim et al. (2018) applied an isoconversional method to differential scanning calorimetry (DSC) data to extract the kinetics of the thermal decomposition of 97.5% hexahydrotrinitrotriazine (RDX), 95% octahydrotrinitrotetrazine (HMX), and boron/potassium nitrate (BPN). Only this latter EM was subjected to isothermal accelerated aging tests at a single temperature of 71°C for 8, 16, 24, and 48 weeks. There was agreement between experimental data and kinetic predictions that, even after 48 weeks, the remaining fraction of BPN was very close to unity.

In the work by Harter et al. (2022), the kinetic analysis of dihydroxylammonium-5,5'-bistetrazolyl-1,1'-diolat (TKX-50), RDX, HMX, hexanitrohexaazaisowurtzitane (CL-20), and pentaerythritoltetranitrate (PETN) was

carried out applying an isoconversional method that fitted thermogravimetry (TG) data slightly better than a model-based method also investigated, but only for TKX-50. Isothermal predictions of the mass loss of each EM were calculated at various temperatures, and the predictions at 100°C were compared with experimental mass loss data of samples subjected to isothermal accelerated aging at the same temperature for 4, 14, and 28 days. Consistency was found between kinetic predictions and experimental aging data.

Li and Cheng (2010) investigated the thermal behavior of nitroguanidine (NQ) using TG/DSC/mass spectrometry (MS)/Fourier-transform infrared spectroscopy (FTIR) analysis. They extracted the kinetics of the thermal decomposition of this EM in the frame of a model-based approach and used the kinetics to simulate the mass loss under isothermal conditions at a temperature of 210°C for a total exposure time (i.e., an aging time) of 30 min. The simulated and TG curves almost overlapped. Isothermal simulations of the mass loss were also performed at lower temperatures (down to 150°C) for a total exposure time of 12 h. Predictions show that before 170°C, the mass loss rose to only 7%, whereas it shifted rapidly to much more after 170°C. This is consistent with the change in the mechanism of the decomposition of NQ in the 160–170°C temperature range deduced by Lee and Back (1988) based on the comparison of the rate constants they obtained from accelerating rate calorimetry (ARC) experiments with literature rate constants derived from measurements performed using techniques other than ARC.

An extensive validation of kinetic predictions against experimental aging data was carried out in Sanchirico et al. (2022a). Specifically, attention was focused on picric acid (PA), an explosive belonging to the class of aromatic nitro compounds (like trinitrotoluene (TNT)). Dynamic DSC experiments were first performed at different heating rates. The gathered thermograms exhibited a single exothermic peak, and there was only one intersection point between curves collected at two different heating rates, confirming the autocatalytic nature of the process under examination (Brill and James, 1993; Long et al., 2002). A kinetic law, $f(\alpha)$, consistent with this nature, i.e., a model of generalized autocatalysis (Kossov and Hofelich, 2003), was thus assumed:

$$f(\alpha) = (z + \alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the conversion, z is the autocatalytic factor, and m and n are the reaction orders. The kinetics (i.e., the kinetic triplet – pre-exponential factor, A , activation energy, E_a , and the parameters of $f(\alpha)$) – were extracted – via a suitable procedure of parameter identification – from DSC data gathered at three different heating rates (2.5, 10, and 20°C min⁻¹). The obtained kinetics were validated against isothermal and further dynamic DSC experiments. Figure 1 shows the comparison between kinetic predictions and experimental data for isothermal conditions.

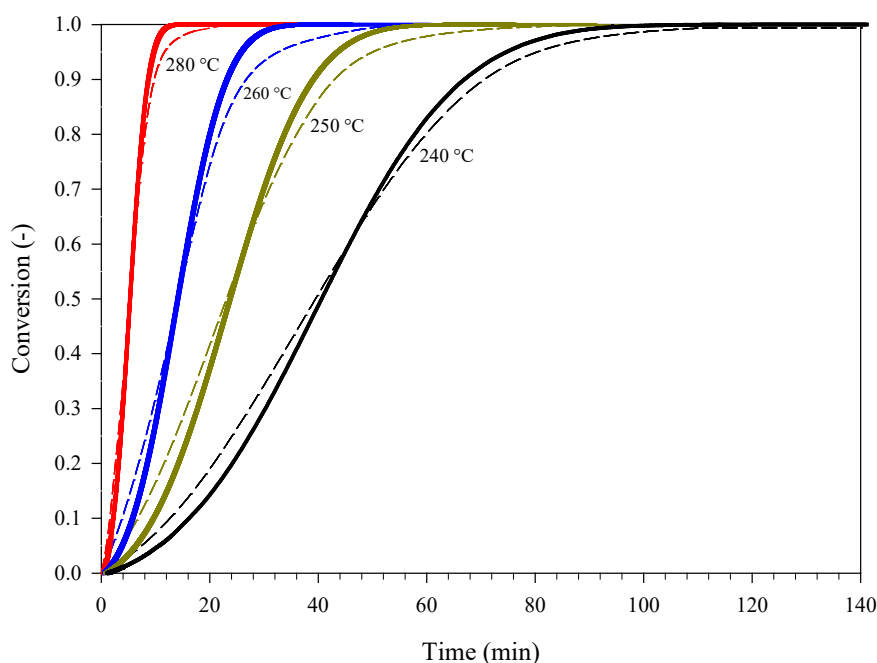


Figure 1: Conversion of PA as a function of time at different temperatures: DSC experiments (dashed lines) and corresponding kinetic predictions (solid lines). (From Sanchirico et al. (2022a)).

After this preliminary validation, kinetic predictions were compared with experimental aging data, i.e., the conversions of aged PA. Such data were obtained for PA subjected not only to isothermal accelerated aging – under such conditions, wide ranges of temperature (from 90 to 230°C) and exposure time (from 25 min to 6 months) were explored – but also to non-isothermal accelerated aging (with temperature following a complex history of variations between 120 and 265°C over a time period of 35 min) and natural aging (during more than 10 years of storage at room temperature). Another element of novelty introduced was the use of high performance liquid chromatography (HPLC) analysis – instead of heat release (Kim et al., 2018) or mass loss (Li and Cheng, 2010; Harter et al., 2022) measurements – to obtain the effective conversion of aged PA. Predictions were found to be in good agreement with experimental data. In this regard, Figure 2 and Table 2 show the comparison under high and low temperature isothermal conditions, respectively. The caption of Figure 2 also details the (high temperature) aging conditions.

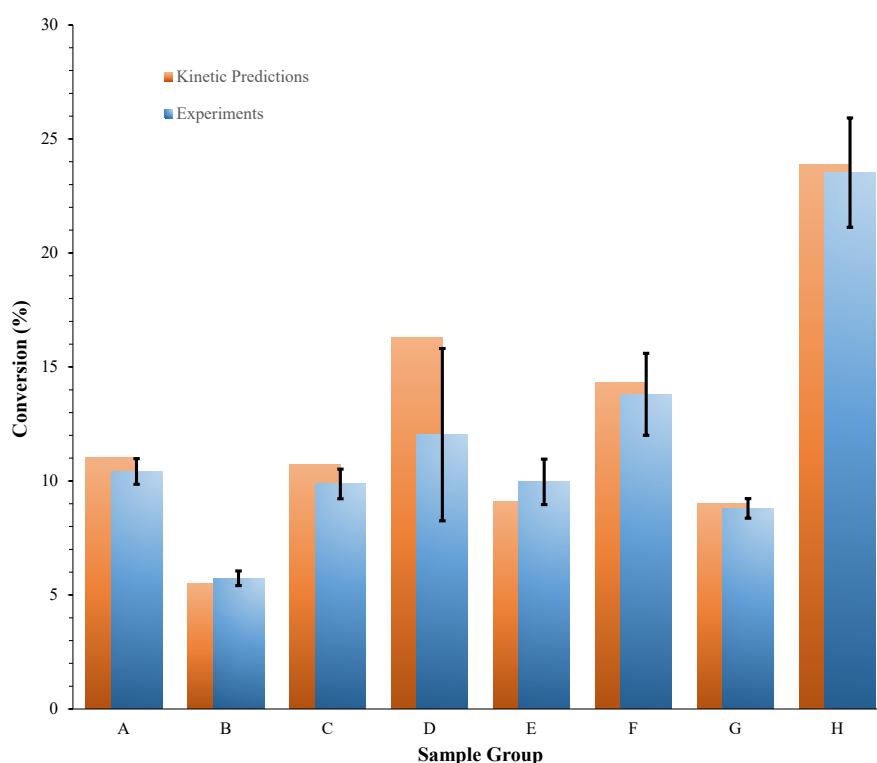


Figure 2: Conversions of PA evaluated using HPLC analysis for different sample groups subjected to high temperature isothermal aging (A: @ 200°C for 180 min; B: @ 210°C for 60 min; C: @ 210°C for 90 min; D: @ 210°C for 120 min; E: @ 220°C for 45 min; F: @ 220°C for 60 min; G: @ 230°C for 25 min; H: @ 230°C for 45 min) and corresponding kinetic predictions. For each sample group, three tests were run. (From Sanchirico et al. (2022a)).

Table 2: Conversions of PA evaluated using HPLC analysis for samples subjected to low temperature isothermal aging and corresponding kinetic predictions. (From Sanchirico et al. (2022a)).

Aging Conditions	Experimental Conversion (%)	Predicted Conversion (%)
140°C for 1 week	5.70	5.75
140°C for 5 weeks	72.10	73.97
90°C for 6 months	<1.00	~0.70

In the case of non-isothermal accelerated aging, a conversion of PA equal to 35.87% was evaluated using HPLC analysis, whereas the corresponding predicted value was equal to 33.53%. The fact that the same sample holder was used in both DSC experiments and accelerated aging tests represents a further point of strength for the performed validation.

For naturally aged PA, a negligible conversion was found – this was consistent with the almost overlap of the dynamic DSC thermograms recorded for a sample of this material and a sample of fresh (i.e., unaged) PA (Sanchirico et al., 2022b) (Figure 3).

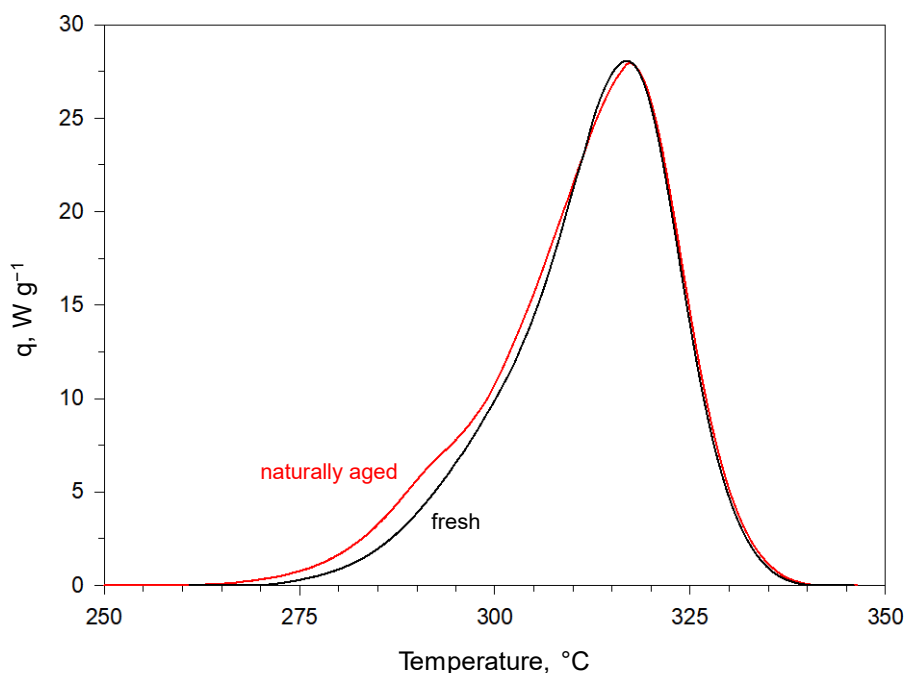


Figure 3: Dynamic DSC thermograms (i.e., specific heat power, q , versus temperature curves) recorded for fresh and naturally aged PA (heating rate of $20^{\circ}\text{C min}^{-1}$). (From Sanchirico et al. (2022b)).

The good agreement between predictions and experimental aging data proves the reliability of the kinetics extracted for PA, also supporting the extension of the adopted model-based approach to the prediction of the shelf life of EMs that, like PA, decompose in an autocatalytic manner.

3. Conclusions

Based on the literature results discussed in the previous section, it can be concluded that the application of the kinetic analysis of decomposition data gathered by using thermal analysis techniques to the shelf life prediction of energetic materials (EMs) deserves further consideration. As a whole, the studies performed so far on this subject, although limited in number, represent a good premise, having shown agreement or (at least) consistency between kinetic predictions and experimental data obtained on actual aged samples. Starting from these studies, future research should broaden the range of investigated EMs, thoroughly assessing the reliability of kinetic predictions against aging data. This assessment involves accelerated aging tests and, therefore, is the most delicate point to deal with. However, the efforts associated with such tests can be suitably optimized through a reasoned planning of the experimental campaign based on indications coming from the kinetic predictions themselves. For example, should test conditions result, even after relatively long aging times (months or years), in values of conversion not detectable by the available measurement techniques, then they would be rejected a priori. The same is true in the case of conversions well above the value corresponding to the failure threshold. From this perspective, the approach presented in this work can be a viable alternative to the standard multi temperature aging method, which, in comparison, is much more time and resource intensive as it requires massive accelerated aging tests.

Nomenclature

A – pre-exponential factor

ARC – accelerating rate calorimetry

BPN – boron/potassium nitrate

CL-20 – hexanitrohexaazaisowurtzitane

DSC – differential scanning calorimetry

DTA – differential thermal analysis

E_a – activation energy

EM(s) – energetic material(s)

$f(\alpha)$ – kinetic law

FTIR – Fourier-transform infrared spectroscopy
 HMX – octahydrotetranitrotetrazine
 HPLC – high performance liquid chromatography
 m – reaction order
 MS – mass spectrometry
 n – reaction order
 NQ – nitroguanidine
 PA – picric acid
 PETN – pentaerythritoltetranitrate

q – specific heat power
 RDX – hexahydrotrinitrotriazine
 TG – thermogravimetry
 TKX-50 – dihydroxylammonium-5,5'-bistetrazolyl-1,1'-diolat
 TNT – trinitrotoluene
 z – autocatalytic factor
 α – conversion

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