

Modified Arrhenius kinetics for double base propellant decomposition: Effect of water

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ABSTRACT

Numerous studies have been conducted on the decomposition mechanisms of cellulose nitrate (NC), a polymer employed in double base (DB) rocket propellants. It is well known that storage temperature affects the lifetime of these energetic formulations. However, less studies have been published on the influence of water. This research examined the role of water on the stabiliser consumption rate during accelerated ageing of a DB rocket propellant, as well as the impact on the shelf life prediction of the energetic formulation. Different volumes of water (0.8, 1.6, 2 and 4 µl/g) were added to the propellant in sealed vials, which were then isothermally aged (70, 80, 90, 100 °C). Analyses of the stabiliser consumption showed a faster decomposition kinetics in presence of water which is indirectly linked to the shortening of the storage life of the NC based propellant by 35 %. For the conditions, an activation energy of 133 ± 4 kJ/mol was reported for the water catalytic decomposition mechanism. A numerical model that included water as a variable was reported to reduce the uncertainty in the determination of the service life of NC based propellant. International standards such as Allied Ordnance Publication 48 should not overlook the effect of water/moisture on the safety of ammunition containing NC and should implement a modified Arrhenius equation.

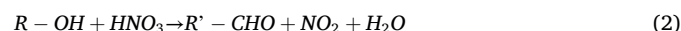
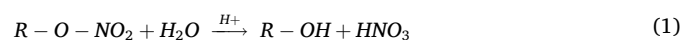
1. Introduction

1.1. Double base rocket propellant decomposition process

Double base (DB) rocket propellants are formulations composed of aliphatic nitrate esters such as cellulose nitrate (NC) and nitroglycerin (NG) [1,2]. The influence of temperature on the stability of these energetic materials has been largely investigated but the impact of humidity is less studied. The presence of water/moisture in this type of propellant is primarily due to the manufacturing process; even with a good drying process, it is possible to find up to 1% w/w of water remaining [3]. Rocket motors usually have environmental seals bonded to the nozzle outlet, usually with polymer resins. However, these resins as well as the O-rings used to seal the rocket motor from the environment can degrade, allowing moisture to enter the system [4,5].

DB rocket propellants undergo either an intrinsic or autocatalytic decomposition process. The intrinsic decomposition starts with the ho-

molytic cleavage of the O–NO₂ bonds, causing NC denitration and a release of nitrogen oxides (NO_x) [6,7]. It always occurs [8] and has two primary mechanisms: i) hydrolysis (Eq. (1) and 2) and ii) thermolysis (Eq. (3)) [9].



According to Vogelsanger [10] and Katoh et al. [11], the presence of water catalyses hydrolysis, which promotes the hydrolytic splitting of the O–NO₂ bond in the nitrate esters. When the released NO_x radicals react with the water in the system, acids are produced which further catalyse the decomposition reaction [12,13].

At low temperatures, such as those seen in propellant storage, hydrolysis is the dominant process, and as the temperature increases, so

Abbreviations: 2-NDPA, 2-nitrodiphenylamine; 2,4-DNDPA, 2,4-dinitrodiphenylamine; DB, Double base; AOP, Allied Ordnance Publication; DPA, Diphenylamine; E_a, Activation Energy; EC, Ethyl centralite; HFC, Heat flow calorimeter; HPLC, High-performance liquid chromatography; N-NO-2NDPA, N-nitroso-2-nitrodiphenylamine; NC, Cellulose nitrate; NG, Nitroglycerin; NO_x, Nitrogen oxides; wc, Water content.

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does the rate of decomposition through hydrolysis [8]. However, with increasing temperature, the second decomposition process known as thermolysis becomes the dominant decomposition mechanism at temperatures over 60 °C [14,15]. It is also worth emphasising that the findings presented by O'Keefe et al. [16] show that the presence of water in NC-based propellants at temperatures above 60 °C does not affect the decomposition kinetics of the thermolysis reaction.

A third decomposition pathway (Eq. (4)) is when the NO_x reacts with the DB propellant, giving rise to more NO_x and, in the case of NC, reducing its molecular mass [8,10]. This autocatalytic reaction results in the generation of more decomposition products, thus massively accelerating the decomposition process [17]. In the literature, there is nothing that indicates Eq. (4) is catalysed by the presence of water.



Autocatalysis generates heat that increases the internal temperature of the propellant and taking into consideration that DB propellants are poor conductors of heat [18,19], if the heat produced by the energetic formulation is greater than the heat it can release, self-ignition can occur. This is more likely to happen with high storage temperatures and large propellant grain diameters [20,21].

Chemical stabilisers are added to DB propellants to slow the autocatalytic decomposition process by reacting with the NO_x produced during the decomposition of the propellant [22,23]. These substances are usually aromatic amines or urea derivatives which, through nitrosation and/or nitration reactions, are able to bind the generated NO_x to their molecular structure [24,25]. A change in concentration of the main stabiliser over time is an indicator of the ageing that is occurring within the energetic formulation [26]. Therefore, the reduction in main stabiliser effectiveness is an indirect measure of the NC-propellant decomposition kinetics. This is studied using accelerated thermal ageing, solvent extraction and quantification via liquid chromatography [27,28].

1.2. Kinetic model of the consumption of stabiliser contained within double base propellants

The controlled ageing of the propellant aims to measure the percentage loss of stabiliser, or stabiliser conversion (α) which is defined in the following equation [29]:

$$\alpha = \frac{\%w_o - \%w_i}{\%w_o - \%w_f} \quad (5)$$

where % w_o , % w_i and % w_f are the percentages of stabiliser present at the start, at time t , and at the end of the test.

In order to study the reaction kinetics of a thermally stimulated process, such as accelerated ageing, the following equation is used [30]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (6)$$

where da/dt is the reaction rate, $f(\alpha)$ is the reaction mechanism function, and $k(T)$ is the reaction rate constant as temperature function which is obtained from the Arrhenius equation below [28]:

$$k(T) = A \exp\left(\frac{E_a}{RT}\right) \quad (7)$$

where A is the pre-exponential factor, E_a is the activation energy (J/mol), T is the temperature expressed in absolute scale (K), and R is the gas constant ($8.314 J/mol K$).

The expressions shown in Eq. (6) can be written in their integral form [31]:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t k(T) dt = A \exp\left(\frac{E_a}{RT}\right) t \quad (8)$$

Table 1

Kinetic mechanism functions [31].

Model	$f(x)$	$g(x)$
Zero order	α	1
First order	$1 - \alpha$	$-\ln(1 - \alpha)$
Second order	$(1 - \alpha)^2$	$\left[\frac{1}{1 - \alpha}\right] - 1$

Table 2

HPLC conditions for stabiliser depletion analysis.

Instrument	Waters Alliance 2695
Module Column	Kinetex 5 μ XB-C18 100 Å @ 30 °C
Mobile phase	40 % CH ₃ CN, 60 % H ₂ O +0.1 % HCOOH
Flow rate	1.5 ml/min
Detector	Waters 996 PDA
Wavelength	254 nm
Injection	10 μ l
Replicates	2 per sample

where $g(\alpha)$ is the reaction mechanism function expressed in integral form.

There are a variety of models for determining the mechanism function (both differential and integral) that depend on the reaction order n which, for NC base propellant decomposition processes, ranges from zero to two [32,33]. Table 1 shows the principal models that depend on the reaction order.

Despite work being done by Eerligh et al. [34] and Teixeira et al. [35] on the effects of water/moisture on the consumption of the stabiliser present in NC-based propellants, no kinetic model applied to propellants has been developed to include the effects of moisture/water on DB propellants.

The aim of this paper was to propose a new kinetic model which includes water for improved life assessment of rocket motors. The level of stabiliser was monitored in a rocket propellant artificially aged at different temperatures and humidity/water concentrations.

2. Material and methods

An extruded DB propellant A (NC 5–57 %w/w, NG 19–46 %w/w, 2-NDPA 1–8 %w/w, and copper oxide 0–3 %w/w) was used in this study. The propellant was previously stored for 15 years (< 20 °C). The propellant was cut from a billet (ϕ 40 mm x 38 mm), sieved (<3 mm) and stored in a vacuum desiccator for 48 h to remove residual moisture. The propellant was then added to 4 ml vials (loading density 0.83 g/cm³) with deionized water (2, 4, 5 or 10 μ l), and sealed. The water volume is reported normalised to propellant mass: 0.8, 1.6, 2 and 4 μ l/g. Propellant A was aged at 70, 80, 90 and 100 °C for up to 49, 36, 10 and 5 days respectively.

For high-performance liquid chromatography (HPLC) analysis, CH₃CN (125 ml) was added to 0.5 ($\pm$ 0.001) g of propellant sample and shaken for 4 h. An aqueous solution of CaCl₂ (25 ml of a 2% w/w) was added to precipitate out the NC. A portion of the supernatant liquid was then filtered through a 0.2 μ m nylon filter into a HPLC vial. The chromatographic conditions used are shown in Table 2. External calibration reference standards 2-NDPA (99.5 % purity) and 2,4-DNDPA (99.5 % of purity) from Sigma-Aldrich Corporation were used. Ageing time is reported as 25 °C equivalence as described in AOP-48 ed2 [36].

3. Results and discussion

3.1. Stabiliser depletion results

Samples (Fig. 1) with the highest water content (4 μ l/g) have a 10-year effective stabiliser content which is at least 35 % lower than

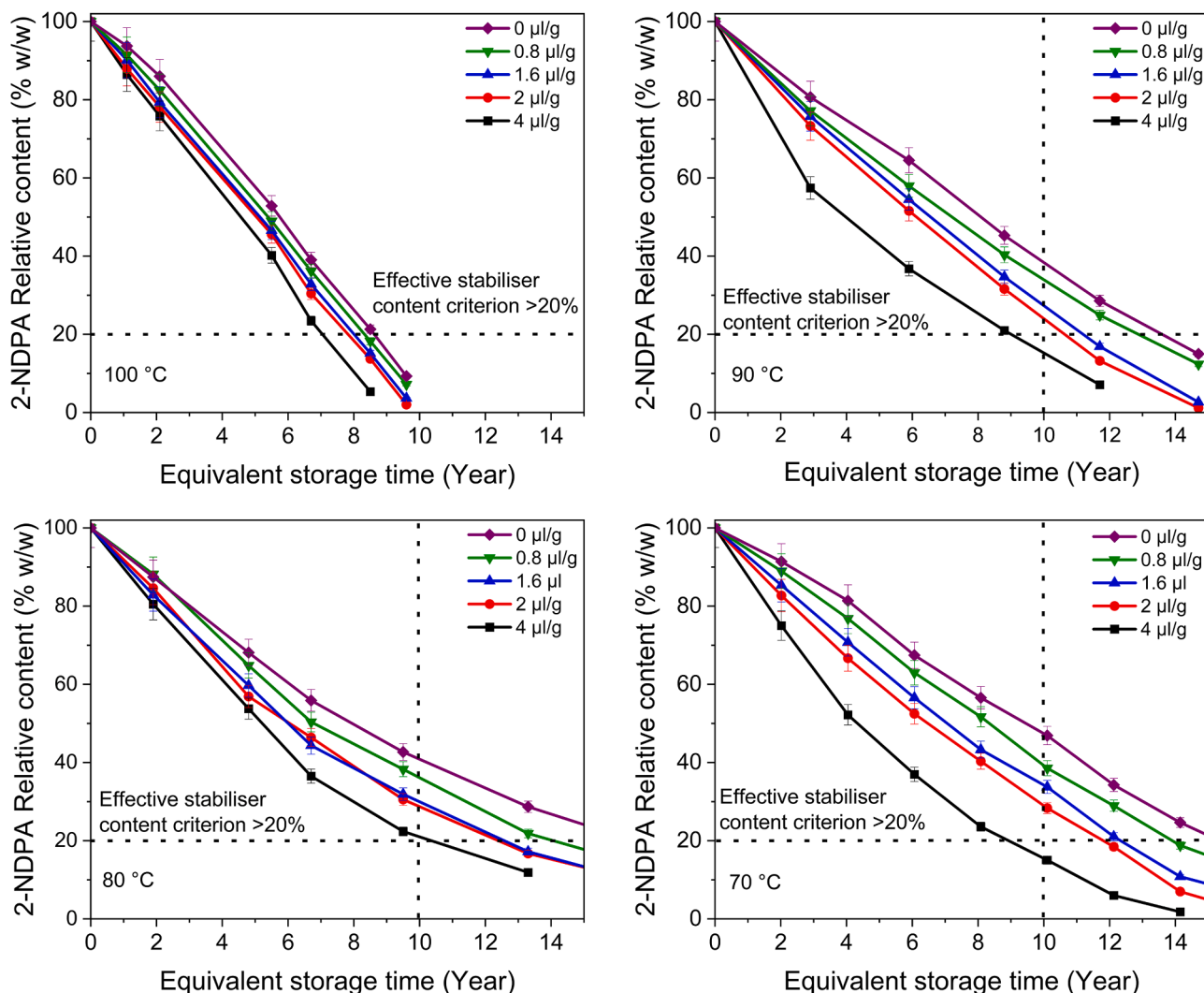


Fig. 1. Influence of water concentrations on the stabiliser depletion (2-NDPA) curves at 70–100 °C. Time plotted as 25 °C equivalent storage time. The dotted lines represent the two acceptance criteria for a 10-year equivalence storage as described in AOP-48 ed2 [36].

samples without added water and they failed the AOP-48 ed2 10-year equivalent storage criteria at all temperatures tested. Samples with a concentration of 1.6 and 2.0 µl/g of water have a very similar shelf life, reaching the permitted effective stabiliser limit in an equivalent period of 12 years. Finally, samples with low water concentration (0 and 0.8 µl/g) have a longer shelf life, being safe for use for more than 14 years.

Stabiliser depletion rate increases with increasing water concentration at all temperatures (70–100 °C), implying that the NC decomposition reaction is catalysed by water [37]. Drzyzga [38], Meng, and Caddy [39] have reported that diphenylamine (DPA) and ethyl centralite (EC) are not hydrolysed in the presence of water; we assume that 2-NDPA is also stable towards hydrolysis.

At 100 °C the 2-NDPA consumption is fastest, and none of the samples tested pass the 10-year 25 °C equivalence ageing criterion. According to Manelis [40] and Brill and Gongwer [41], for temperatures above 100 °C, the dominant mechanism of decomposition for DB propellant is autocatalysis, a reaction characterised by increased NO_x production (see Eq. (4)), which explains the accelerated consumption of the stabiliser even at an effective stabiliser concentration [37].

Fig. 2 shows that the formation of one of the secondary stabilisers (2,4-DNDPA) between 70 and 100 °C has very similar trends than 2-NDPA. The higher the water content in the samples, the higher the concentration of the secondary stabiliser 2,4-DNDPA. It is worth noting that in all cases, the samples with the highest water content (4 µl/g) have

the fastest rate of 2,4-DNDPA production.

3.2. Stabiliser depletion kinetics

Based on previous reported work stabiliser consumption is considered as a first order model [33,42]. Therefore, substituting the first order function shown in Table 1 into Eq. (8):

$$-\ln(1 - \alpha) = kt = A \exp\left(-\frac{E_a}{RT}\right)t \quad (9)$$

The stabiliser consumption conversion is determined from the failure criterion set by AOP-48 ed2 ($\alpha=20\%$ effective stabiliser content) and t is the time to reach α . Table 3 shows the values of k obtained for the different temperatures at which the samples were tested with a water content of 0.8 µl/g water.

The results obtained from the kinetic analysis (Fig. 3) show that the activation energy (133 ± 4 kJ/mol) for the five different water concentrations are equivalent. The literature [8,43] indicates that the decomposition mechanism cannot be hydrolysis, since this process occurs with $E_a > 120$ kJ/mol, therefore thermolysis is more likely. However, as previously discussed, thermolysis is not influenced by water, suggesting the autocatalytic reaction is the main reaction observed. [16, 37].

Waterman [44] and Li et al. [45] have employed a combined model

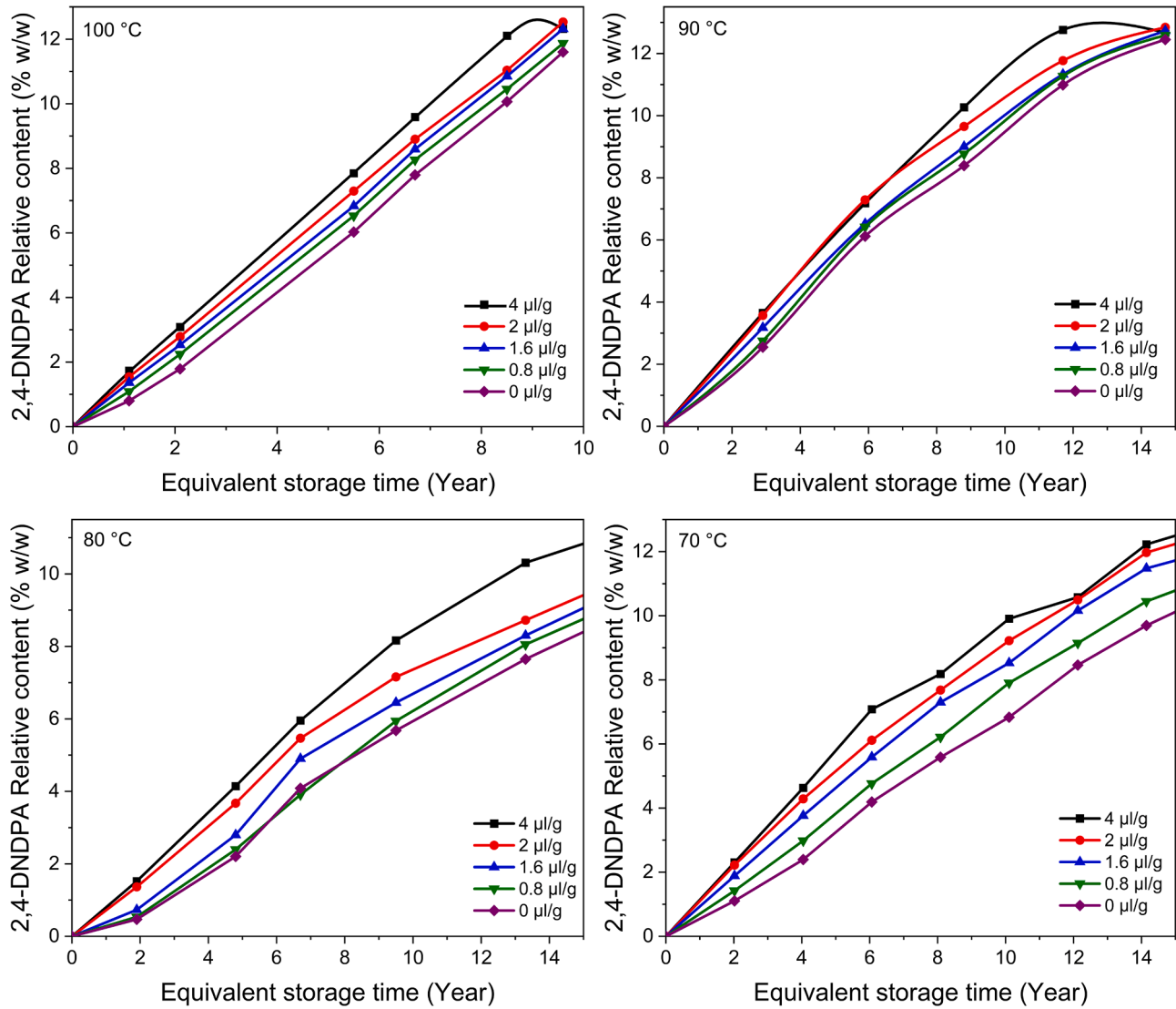


Fig. 2. Influence of water concentrations on the secondary stabiliser product (2,4-DNDPA) concentration at 70–100 °C. Time plotted as 25 °C equivalent storage time.

Table 3
Kinetic parameters for 0.8 µl/g samples at different temperatures.

Temperature (°C)	Time to reach 20 % effective stabiliser (s)	k (s ⁻¹)	$\ln k$ (s ⁻¹)
100	95,040	2.35e-6	-12.96
90	380,160	5.91e-7	-14.34
80	1,261,440	1.78e-7	-15.54
70	4,168,800	5.37e-8	-16.74

taking into account moisture/water content to study the degradation and stability of different materials related to pharmaceutical and food industry. The modified Arrhenius equation used is as follow:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) + (C \cdot wc) \quad (10)$$

where C is the water content constant and wc is the water content.
The findings in Fig. 4 validate that there is a strong connection

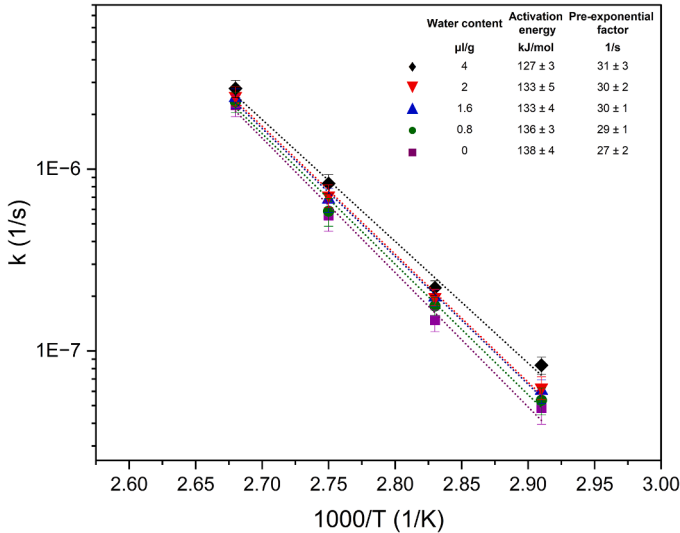


Fig. 3. Influence of water concentration on activation energy of stabiliser depletion (70–100 °C).

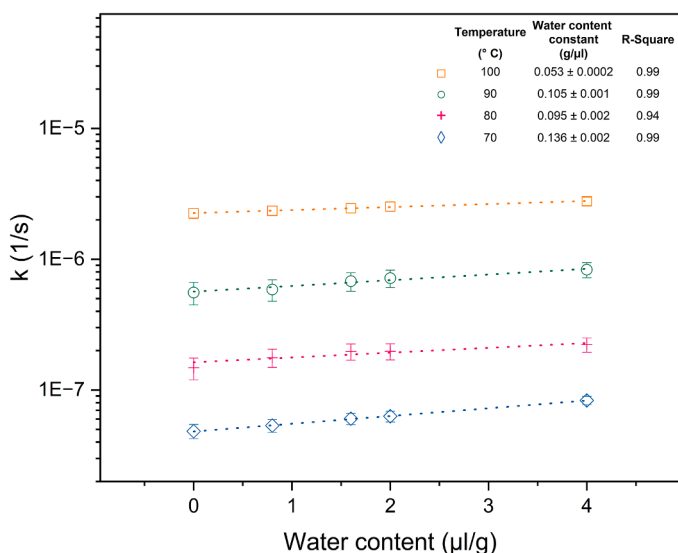


Fig. 4. Relationship between the rate constant and the water content at various temperatures.

Table 4

Comparison between activation energies obtained from the HFC and the stabiliser consumption tests.

Test	E_a (kJ/mol)
HFC [37] Propellant A. Aged at 80–100 °C: 6, 12, 17, and 22 g/m ³ absolute humidity	131 ± 3
Stabiliser consumption Propellant A. Aged at 70–100 °C: 0.8, 1.6, 2 and 4 μl/g normalised water content	133 ± 4

between k and water content in the samples in the temperature ranges used in the experiments, hence the value obtained for the moisture constant C is 0.097 ± 0.0015 g/μl. As a result, Eq. (10) is valid for establishing the stabiliser depletion kinetics under temperature-water content conditions. By substituting the data from the previous graphs into Eq. (10), the reaction rate equation is as follows:

$$\ln|k| = -\frac{133 \text{ kJ/mol}}{RT} + \ln|29| + [0.097 \text{ g} / \mu\text{l} \cdot \text{WC}] \quad (11)$$

The activation energy is equivalent to previously published heat flow calorimeter (HFC) data [37] of the same propellant samples (Table 4).

4. Conclusions

Water is a significant factor in sealed vial experiments in which the autocatalytic secondary reaction mechanism plays an important role in the lifetime of the double base rocket propellant. The reduction in main stabiliser is an indirect method for assessing the chemical life for NC propellants. The result from this methodology shows that increasing water concentration decreases the life of the propellant by 35–43 %. Accelerated ageing has shown that the presence of water promotes autocatalysis as the main decomposition reaction of a DB rocket propellant. Samples with the highest water concentration (4 μl/g) decreased in life from 14 years to only 8 years (25 °C equivalency), compared to no added water.

This study has shown that it is necessary to consider more than just temperature when analysing the life of NC propellants. We proposed a modified Arrhenius equation including the effect of water for improved life assessment of rocket motors. Currently, standards such as Allied Ordnance Publication (AOP)–48 ed2 do not consider water/moisture presence as a major factor in the decomposition of NC-based propellants.

Implementing a modified Arrhenius equation that includes the water as a variable reduces the uncertainty in the chemical and the mechanical degradation of propellant, increasing the safety, life and reducing the overall costs of the rocket motor.

CRedit authorship contribution statement

Alonso Romero Jabalquinto: Writing – original draft, Validation, Conceptualization. **Nathalie Mai:** Writing – review & editing, Supervision, Conceptualization. **Samira Belghiche:** Supervision. **Philip P. Gill:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alonso Romero Jabalquinto reports financial support was provided by Mexican National Council of Sciences and Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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