The Prediction of CMDB Propellant lifetime Based on Arrhenius accelerated model, Berthelot’s equation and Multi-step Prout-Tompkins Model

Qiong Wang*, Yan Gu, Jiaojiao Du, Lin Jia, Linjun Zhang
Xi’an Modern Chemistry Research Institute, Xi’an city, ShaanXi Province, China

*Corresponding author email: wq204s_xa@163.com

Abstract. Different models were provided to predict the storage lifetime of propellants more accurately. The stabilizer was recognized as a vital parameter for double based propellants’ storage lifetime estimation. The stabilizer contents of a certain RDX-CMDB propellant were traced during the accelerated aging tests. Based on that, the safe storage lifetime of this propellant were predicted using the Berthelot’s equation, Arrhenius accelerated equation and the advanced kinetic model, respectively. The predicted results were compared and the causes were analysed. It found that the biggest disadvantage of Berthelot’s equation and Arrhenius accelerated equation is that the predicted results are significantly affected by the original data. In details, the minor difference of original data will bring tremendous errors when extrapolating to normal temperature. The general model which can be used to depict complex reactions adopted in AKTS software was preferred compared to reaction order (RO) model and Prout-Tompkins (PT) model.

Keywords: safe storage lifetime, stabilizer content, CMDB propellant, accelerated model.

1. Introduction
The stability of explosives and propellants containing self-reactive material such as nitrocellulose has been a main focus for propellant safety engineer [1~9]. Usually, the stabilizer depletion was considered as an important safety index for most propellants containing nitrocellulose [10~13]. Based on the stabilizer depletion data from accelerated aging test at different temperature, the parameters t25 and T10 were calculated as the standard AOP-48 advised [14]. Usually, three methods viz. Berthelot’s equation, Arrhenius accelerated equation and kinetic model calculation were used. The t25 was obtained by extrapolation directly based on the experimental data and linear relation between lnt and T or 1/T for the two former methods. The modified Prout-Tompkins (PT) model [15] with the formula dα/dt=k (1-α)n was advised [16] to depict the process including catalytic reaction based on the comparative analysis of PT model and RO model. According to the report [17], the RO model can’t depict the reaction for single based propellants correctly. The PT model which can depict simple n-order reaction and autocatalytic reaction simultaneously is a better choice, due to consumption mechanism of stabilizer for most propellants is unknow and lower requirement of the PT model for the experiment.
Berthelot’s equation was considered better than Arrhenius equation by many investigators [18] in view of the storage time predicted by the former method is shorter than that obtained from the latter. But now the accurate prediction of safe storage lifetime of propellants is the key point in order to guarantee the storage safety and save cost simultaneously. In this paper, the storage lifetime of a RDX-CMDB propellant was predicted using three methods, and the difference was analyzed specifically.

2. Experiments and methods

2.1. Artificial aging test and measurement of stabilizer content
RDX-CMDB propellant prepared by the Xi’an Modern Chemistry Research Institute was accelerated in the oven at 55°C, 65°C, 75°C and 85°C, respectively. The samples were put into sealed glass vessels during test and were kept in a desiccator before and after the test. The centralite/ stabilizer was 2-nitrodiphenylamine (2N-DPA) and 1, 3-dimethyl-1,3-diphenlurca (C2) mixture. The effective centralite/ stabilizer content was determined by standard bromine method: GJB 770B-2005-210.1 and 770B-2005-210.1, which are equivalent to MIL-STD-286C-210.1.4 and 202.2.3, respectively.

2.2. Advanced kinetic analyses
Data analysis was performed using AKTS-Thermokinetics software, more information can be found in the company’s official homepage http://www.akts.com. A general form of reaction rate as follows based on Pérez-Maqueda formula [19] was advised by B. Roduit [16].

\[
\frac{da}{dt} = \sum_{i=1}^{l} k_i (1 - \alpha)^{n_i} \alpha^{m_i}
\]

(1)

Not only can this equation be use to depict the simple n-order reaction and autocatalytic reaction when i, n and m were given different values, but also can depict the process composed of multi-steps. The feasibility of predicting the stability of propellant using AKTS Themokinetics were verified by Roduit B. [16].

3. Results and discussions
The original data about the time and the stabilizer content were listed in table 1.

3.1. The safe storage time prediction of the propellant using Berthelot’s equation and Arrhenius’ accelerated equation
The earliest reference about Berthelot’s equation we can get is the paper reported by Garman N. S [18], in which it said that a French delegation at one NATO meeting suggested that kinetic interpretation of decomposition propellant can be interpreted by the use of Berthelot’s law of deterioration phenomena. From that we can’t say the Berthelot equation is just an empirical equation or a law based on physical-chemistry model like Arrhenius rate equation, but both equations are only two of many relationships between reaction rate constant K and temperature T [20]. In the paper [18], it declared that the Berthelot’s equation can’t be used to depict propellants like M10 single-based formulation, and revealed that many investigators used both methods Berthelot equation and Arrhenius equation, and the safe storage life predicted by Arrhenius equation is much longer than that gained from Berthelot equation. The coefficient gamma (γ10) corresponding to the increase of the reaction rate for a temperature change of 10 oC for M1, M6, M5 and M7 were 3.83, 3.29, 3.75 and 4.49 respectively. To verify the agreement between the predicted results and the decomposition under normal storage conditions, they provided seven comparative data [18]. From the data we can see the stabilizer loss is less than 15% which is far below the critical point 50% appointed in many documents. Its’ out of question that the storage time predicted would be longer or shorter than the actual storage time. More importantly, the difference between the predicted time and actual storage time will become larger when the stabilizer loss increases from 5% to 50%. It will bring great adverse effect to the accurate prediction of safe storage life of propellants. Due to the different relationship between logarithm of time and T for Berthelot’s equation
and Arrhenius accelerated equation, the time predicted from Arrhenius equation is much longer than that obtained from Berthelot equation.

### Table 1. Stabilizer Content at different time and test temperature for RDX-propellant

| T_a (55 °C) | T(65°C) | T (75 °C) | T (85 °C) |
|-------------|---------|-----------|-----------|
| t^b (day)  | t (day) | t (day)   | t (day)   |
| 0           | 0       | 0         | 0         |
| 30          | 2       | 1.96      | 13        |
| 59          | 1.9     | 20        | 1.9       |
| 164         | 1.6     | 30        | 1.62      |
| 227         | 1.34    | 50        | 1.29      |
| 306         | 1.13    | 68        | 1.04      |
| 361         | 0.98    | 88        | 0.74      |
| 0           | 2       | 0         | 2         |
| 6           | 1.83    | 1         | 1.88      |
| 8           | 1.64    | 2         | 1.64      |
| 21          | 1.12    | 3         | 1.48      |
| 30          | 0.76    | 4         | 1.07      |
| 5           | 0.77    | 5         | 0.77      |

Note: a) T is temperature; b) t is ageing time; c) C is stabilizer content remained in propellants;

To quantitatively and visually compare the difference between the predicted time using Berthelot’s equation and Arrhenius equation, the safe storage time for the RDX-propellant was calculated based on the premise that the critical point of stabilizer content is 50%.

The time periods were 379.22 days, 70.88 days, 24.18 days and 4.35 days respectively for propellant accelerated at 55°C, 65°C, 75°C and 85°C. Based on those data and formula (7) and (8), the Berthelot’s equation and Arrhenius’ equation were obtained as follows.

\[
lgt = 22.813 - 0.0618T \quad (2)
\]

\[
ln t = 16710.39267 / T - 45.05571 \quad (3)
\]

The R² were 0.989 and 0.987 respectively. From equation (9) and (10), the safe storage time of this propellant under 20°C, 25°C and 30°C were 136.1 a, 66.8a and 32.8 aand 422.9 a, 162.6 a and 64.5 a respectively. In order to have an visual impression on the difference of storage time predicted by those two methods, the time ratio of Arrhenius’ equation to Berthelot’s equation was showed in figure 1.

![Fig. 1 The ratio of time predicted by Arrhenius’ equation to Berthelot’s equation](image)

From the figure 1, it can be found that the time ratio is around 1 in a very small temperature range from 50 oC to 90oC. However, as temperature exceeds this range, no matter it increases or decreases, the time ratio increases quickly. This phenomenon is caused by extrapolating blindly from limited small data to unknown region.

Both methods viz Berthelot’s equation and Arrhenius’ equation predict the safe storage time without consideration of the reaction mechanism. For deep understanding the influence of the experiment errors on the predicted storage time, the time period was treated by approximation. In details, the time periods after which the stabilizer consumed 50% at 55°C, 65°C, 75°C and 85°C were rounded off as 379 days,
71 days, 24 days and 4 days. After this treatment, the safe storage time of this propellant at 20°C, 25°C and 30°C predicted were 173.9a, 83.3a and 39.8a by Berthelot’s equation and 566.4a, 210.4a and 80.8a by Arrhenius’ equation. Compared to the calculated results above, it’s easy to notice that significant differences were caused by the minor treatment of original data. That is exactly the disadvantage that those both methods have in common. In order to investigate the influence of temperature fluctuation, which is a common phenomenon in real artificial aging tests, on the precision of predicted results, the storage time under different conditions were calculated. The temperature deviation in the test is assumed to be ±0.5°C, and the results were listed in table 2.

| Ta(℃) | tb(day) | method       | Storage time (years) | Error/% |
|-------|---------|--------------|----------------------|---------|
|       |         |              | 30°C | 25°C | 20°C | 30°C | 25°C | 20°C |
| 55,65,75,85 | 379.22, 70.88, 24.18, 4.35 | Berthelot   | 32.8 | 66.8 | 136.1 | 21.3 | 24.7 | 27.8 |
|         | 379, 71, 24, 4               | Arrhenius   | 64.5 | 162.6 | 422.9 | 20.7 | 22.5 | 23.9 |
| 55.5,65.5,75.5,85.5 | 379.22, 70.88, 24.18, 4.35 | Berthelot   | 39.8 | 83.3 | 173.9 | 21.3 | 24.7 | 27.8 |
|         |                                  | Arrhenius   | 80.8 | 210.4 | 566.4 | 25.3 | 29.4 | 33.9 |
| 54.5,64.5,74.5,84.5 | 379.22, 70.88, 24.18, 4.35 | Berthelot   | 34.3 | 70.7 | 145.9 | 4.6  | 5.8  | 7.2  |
|         |                                  | Arrhenius   | 67.3 | 171.9 | 453.6 | 4.3  | 5.7  | 7.3  |
| 55,65,75,85 | Original data | AKTS        | 44.2 | 113.8 | 302.3 |       |       |       |
| 55.5,65.5,75.5,85.5 | Original data | AKTS        | 47.7 | 124.6 | 332.3 | 7.9  | 9.5  | 9.9  |
| 54.5,64.5,74.5,84.5 | Original data | AKTS        | 39.0 | 97.1 | 258.4 | -11.8 | -14.7 | -14.5 |

Notes: a) T is temperature; b) t is ageing time; c) error was calculated on the assumption that the storage time predicted using temperature data 55,65,75,85 and time data 379.22, 70.88, 24.18 and 4.35 is the authentic value for the Berthelot’s equation and Arrhenius’ equation method, and the storage time predicted using temperature data 55,65,75,85 and original time is the authentic value for AKTS software.

It can be seen from table 2 that the errors varied from 21% to 34% when the test time was rounded off using Berthelot’s equation and Arrhenius’ equation, and from 4% to 31% when the test temperature fluctuated ±0.5°C.

3.2. The safe storage time prediction of the propellant through advance kinetic model

The consumption of stabilizer in this propellant can be described by the following equation:

\[
\frac{d\alpha}{dt} = \exp(36.123) \exp \left(-\frac{142100}{8.315T}\right) (1 - \alpha)^{0.585}
\]

(4)

From equation (11), it can be seen that the consumption of stabilizer in this propellant can be described in autocatalytic reaction model. Based on the reaction model equation (11), the reaction progress vs the corresponding safe storage time can be calculated under different temperatures. In this paper, the stabilizer depletion vs storage time of this propellant under 20°C, 25°C and 30°C were calculated with the confidence interval 95 %, and the typical results under 20 °C were given in figure 2.
Fig. 2 Simulation of reaction progress vs storage time at 20 ℃. The black denotes the simulated data, the blue and the red denotes the upper and lower limitation with 95% confidence level, respectively.

The safe storage time after which the stabilizer content will be consumed 50% were 302.3a, 114.2a and 44.2a respectively for propellant at 20℃, 25℃ and 30℃. It lies between the time predicted by Berthelot’s equation and Arrhenius’ equation, and it is closer to data predicted by Berthelot’s equation. Obviously, the results predicted by AKTS software are more conservative than that calculated using Berthelot’s equation.

In order to investigate the influence of experimental conditions on the accuracy of the storage time prediction, the temperate fluctuation was also set ±0.5℃. The safe storage time of the propellant at 20℃, 25℃ and 30℃ were calculated, and the results were listed in table 2. From table 2, we can see that as temperature changed, the error varies from 8% to 15% which is much smaller than that brought by Berthelot’s equation and Arrhenius’ equation.

4. Conclusion
All methods mentioned above just used a phenomenological mathematical model to fit the experimental data without any mechanism information. On the consideration of the fact that the predicted results can be significantly influenced by the original data and it will bring forth great errors when extrapolating, it’s preferred to use AKTS rather than Berthelot’s equation and Arrhenius accelerated equation when predicting the stability of materials especially for propellant. However, we should keep this in mind that the result predicted by AKTS is also short of confidence.

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