

KINETIC MECHANISM ON THERMAL DEGRADATION OF A NITRATE ESTER PROPELLANT

Muthanna R. Hamad

Chemical Engineering Faculty, Military College of Engineering – Iraq

ABSTRACT

The thermal degradation of a double-base propellant has been studied to elucidate the rate determining steps and the kinetic mechanism in a wide range of temperatures (60°C-200°C) by using modified Taliani test, thermogravimetry (TG), and temperature-varied Abel (TVA) test. The results indicate that the degradation process consists of two major reactions, homolysis and autocatalysis, depending on temperature and total pressure due to evolved gases. The activation energy for the homolysis was obtained to be 35-37 kcal/mol from Taliani TVA tests, which fall in the range of the bond dissociation energy of the weakest bonds RO-NO₂. The activation energy for the autocatalysis was determined to be 46-49 kcal/mol from Taliani and TG methods. Those values observed for the two key reactions are totally opposite to reported values in the earlier literature. The temperature dependence of the reaction rates obtained in this study implies that the homolysis is the rate-determining step in the lower temperature range, the autocatalysis in the higher temperature range.

INTRODUCTION

In recent years there has been an increase in interest in the aging characteristics of high-energy smokeless rocket propellants. A double-base propellant is one of the commonly used matrices of the smokeless propellants. An understanding of the kinetic mechanism on thermal degradation of nitrate esters will permit more accurate aging-prediction for advanced smokeless propellants.

Accelerated aging of propellants is an attempt to reduce the time scale by storing the propellant at elevated temperature^[1-3] so that prediction can be made in shorter times; however, those obtained from extrapolation of the Jesuits to normal storage temperatures do not always agree with the changes observed under normal conditions^[4]. This is mainly due to the lack of adequate knowledge of the kinetics and mechanisms of thermal degradation of nitrate esters used as the basic ingredients of smokeless propellants.

Earlier works on the thermal degradation on nitrate esters revealed, that the predominating reactions are homolytic cleavage of the weakest RO-NO₂ bonds and autocatalytic reaction due to NO₂ evolved. An excellent survey article^[5] has recently appeared on the chemistry of nitrate esters. An observed activation energy (43-47 kcal/mol) has been

believed to be for the homolysis; however, it is somewhat higher than the expected values (35-40 kcal/mol)^[6], and no satisfactory explanation has been put forward in the literature. On the other hand, the observed low activation energies (31-38 kcal/mol) have been attributed to the autocatalysis, since autocatalytic effects generally tend to give low rather than high activation energy.

This paper aims to elucidate the rate-determining step of the thermal degradation of a double-base propellant over a wide range of temperature from 60°C to 200°C, and to determine the Arrhenius parameters for the purpose of more accurate estimation of the aging characteristics of double-base propellants. A thermogravimetry (TG), modified Taliani (manometric) test, and temperature-varied Abel (TVA) test were employed.

EXPERIMENTAL

The composition of a double-base propellant testes was 16.0% nitroglycerin (NG), 79.3% nitrocellulose (NC), 2.6% diethylphthalate (DEP), 2.1% 2-nitrodiphenylamine (2-NDPA). The sample was manufactured by a base-grain process. The dimensions of the sample were 1 mm in length and 1 mm in diameter. For thermogravimetry (TG/DTG) one base grain

of ca. 1 mg in weight was used. In Taliani test 1 g, of the sample was used-

Kinetic studies were carried out with the combined TG/DTG (up to 250°C), Taliani test (110°C-140°C) and the TVA test (60°C-80°C).

Shimadzu TG-20 vertical type thermobalances one of the Cahn-type electromagnetic balances, and auto-recording Taliani test apparatus manufactured by Kuramoti Science Co. were employed. The KI-starch papers used in the TVA test were provided by Toyo-Rosi Co. TG/DTG measurements were conducted under nitrogen flowing condition (50 cm³/min). Taliani test was carried out under nitrogen atmosphere, which was attained by repeating evacuation of air and refilling of nitrogen three times.

RESULTS AND DISCUSSION

Typical pressure-time curves obtained by Taliani test are shown in Fig. 1. These curves indicate that the overall reaction may proceed in self-accelerating manner. It is well-known that the thermal degradation of nitrate esters may proceed with two processes; a first order reaction (homolysis) and an auto catalysis. Thus the overall reaction rate can be expressed as the sum of the kinetic expression [7] used in the deduction of Arrhenius parameters from the pressure curves shown in Fig. 1. Replotting of pressure curves gave straight lines as depicted in Fig. 3. These observations provide a sound evidence for the view proceeds via homolysis and autocatalysis (k_a) and the intercept gives the logarithm of the ratio of rate constant for homolysis (k_h) to the (k_a). After k_a has been obtained, k_h may be calculated from [the second equation in Fig. 3. The kinetic parameters obtained are listed in Table 1.

A number of independent investigators have reported the values of E and A for the thermal decomposition of NC, NG, and NC+NG. The range of the reported values of E and A are also tabulated in Table 1 as a reference. It is noteworthy that the values observed are totally opposite to those reported by others. It should be, however, pointed out that our activation energy for the homolysis falls; well in the range of the theoretical activation energies (35-40 kcal/mol), which equal to the bond dissociation energy of

RO-NO₂ bond.

Whereas the observed high value of E and A for the autocatalysis can not be simply explained. Further investigation will be needed to clarify the kinetic mechanism of the autocatalysis. In order to elucidate the characteristic features of the complex degradation processes of a double-base propellant, the calculated reaction rates are plotted against the reciprocal of temperature in Fig. 4. Three solid lines represent reaction rates of the reaction rate of the autocatalysis is a product of rate constant and pressure of evolved gases. A dotted line represents the rate curve due to the homolysis.

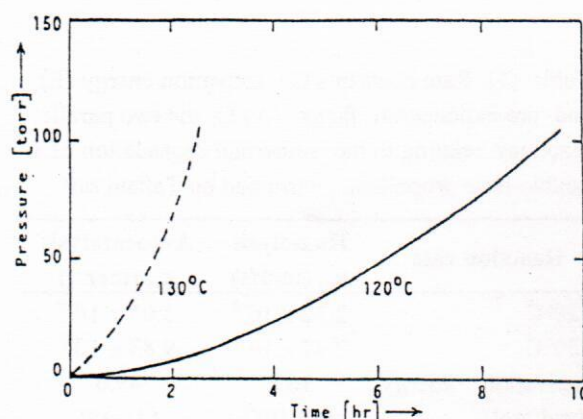


Fig. (1) Cumulative product pressures on the thermal degradation of the double-base propellant in nitrogen at 120°C and 130°C obtained from Taliani test

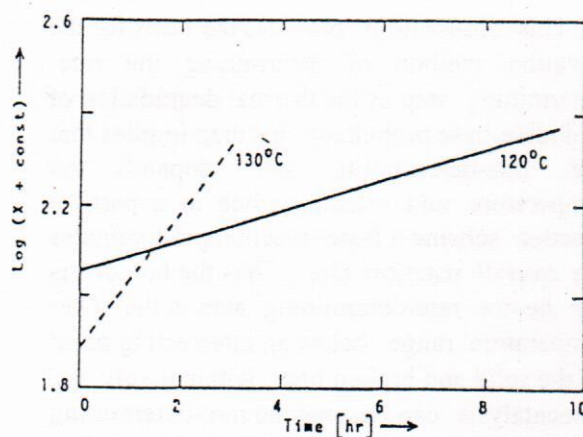


Fig. (2) Kinetic analysis of a typical parabolic pressure-time curve (as depicted in fig. 1) based on the assumption that the overall reaction consists of a pseudo-zeroth order homolytic reaction and a pseudo-first order autocatalysis (cf. Fig. 3)

Calculation	Definitions
Rate of pressure increase:	k_h = Rate Constant for Homolysis
	k_a = Rate Constant for Autocatalysis
$\frac{dX}{dt} = k_h + k_a \cdot X$	X = Pressure generated [torr]
	t = Time [s]
$\log(X + \text{const}) = \log(k_h/k_a) + k_a \cdot t/2.303$	A_h = Pre-exponential Factor for Homolysis [torr/s]
	A_a = Pre-exponential Factor for Autocatalysis [torr/s]
	E_h = Activation Energy for Homolysis [cal/mol]
	E_a = Activation Energy for Autocatalysis [cal/mol]
$k_h = A_h \exp(-E_h/RT)$	R = Universal Gas Constant (1.987 [cal/mol K])
$k_a = A_a \exp(-E_a/RT)$	T = Absolute Temperature [K]

Fig. (3) Determination of kinetic parameters from Taliani test (Ref. 7).

Table (1) Rate constants (k), activation energy (E), and pre-exponential factor (A) for the two parallel reactions relating to the isothermal degradation of a double-base propellant determined by Taliani test

Reaction rate	Homolysis	Autocatalysis
	k_h , (torr/s)	k_a , (torr/s)
120°C	2.32×10^{-3}	2.07×10^{-5}
130°C	7.47×10^{-3}	9.83×10^{-5}
Activation energy (kcal/mol)	36.8 (44-50)*	49.0 (31-38)
Pre-exponential Factor, (torr/s)	6.79×10^{17} (10^{19} - 10^{21})	3.69×10^{22} (10^{12} - 10^{16})

Values in parenthesis denote the range of the values reported by earlier workers

This observation provides the basis for the isolation method of determining the rate-determining step of the thermal degradation of a double-base propellant; this map implies that the rate-determining step depends on temperature and pressure since in a parallel reaction scheme a faster reaction predominates the overall reaction rate. Thus the homolysis can be the rate-determining step in the lower temperature range below an intersecting point of the solid and broken lines. Alternatively, the autocatalysis can become the rare-determining step at the temperatures above an intersecting point. Consequently, the lower (ca. 37 kcal/mol) activation energy should be obtained in the lower temperatures range and the higher (ca. 49 kcal/mol) activation energy are expected to be obtained in the higher temperature range. Bearing these predictions

in mind we attempted confirmatory experiments by using TG/DTG and TVA tests to avoid the danger of making mechanistic deduction on limited information.

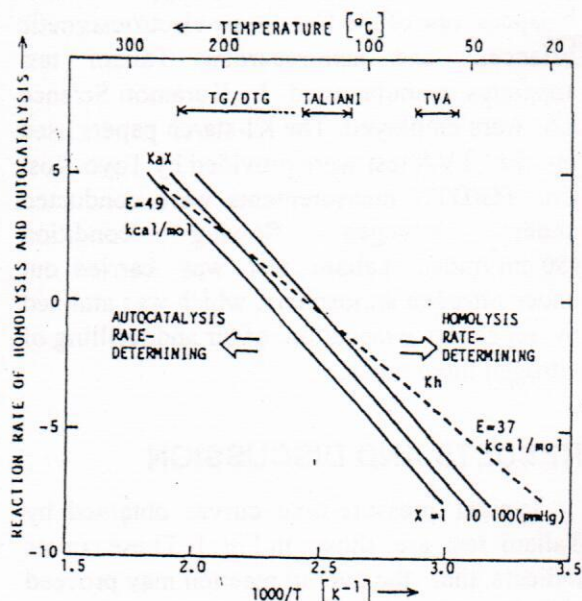


Fig. (4) Map of rate-determining reactions of thermal degradation of a double-base propellant as a function of temperature and pressure.

As can be seen in Fig. 5, double peaks were observed in the DTG curves of two double-base propellants having different NC/NG ratio. No one [8-10] has reported those separated peaks in DTA or DSC studies of double-base propellant probably due to [he fact that one strongly exothermic peak overshadows a weakly exothermic peak due to NC or NG. The temperature at which the first DTG peak appears was lower by ca. 10°C than that of the second peak.

In order to assign the observed DTG peaks, two samples having NC/NG ratio of 1.4 and 5.0 were employed. Figure. 5 shows a direct comparison of the DTG thermograms of the two samples. The relative rate of weight-loss of the first peak to the second one seems to be almost inversely proportional to the NC/NG ratio. Thus it can be concluded that the first DTG peak is due to the thermal decomposition of NG and the second peak to NC. It should be noted that the NG decomposed at lower temperature compared to NC. From the TG/DTG curve shown in Fig. 5, gradual weight-loss of the double-base propellant containing higher amount of NG was observed

to obtain 46 kcal/mol for NG and 47 kcal/mol for NC, which agree well with the anticipated value (49 kcal/mol) from Fig.4. The observed identity of the Taliani-test results with those obtained by thermogravimetry provides evidence that the rate-determining step is autocatalysis with activation energy of 46-49 kcal/mol.

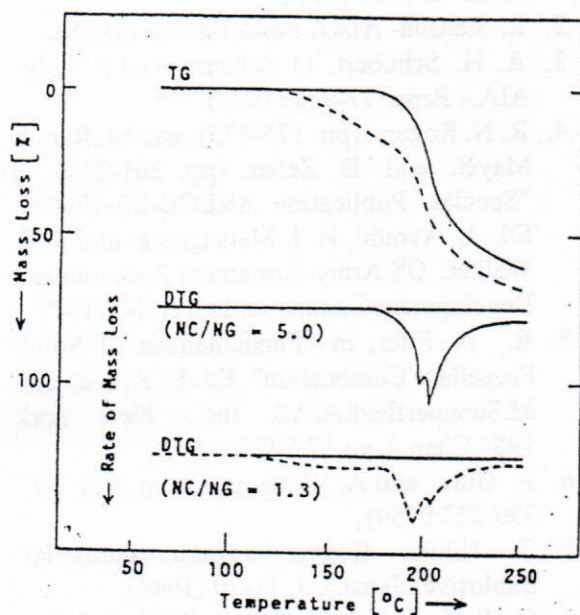


Fig. (5) Dependence of shape of DTG curves of double-base propellant on NC/NG ratio: the first peak is due to the decomposition of NG and the second peak is due to the decomposition of NC. Heating rate: 2°C/min; sample weight: 2 mg.

In order to clarify the kinetic mechanism of the low temperature decomposition the TVA test was conducted. In the TVA test, time for NO^{\wedge} generation to a certain concentration was obtained as a function of temperature. The waiting time observed was plotted against the reciprocal temperature according to the Arrhenius rate law. A straight line was obtained in this plot as depicted in Fig. 7. The slope of the straight line yields the activation energy on the assumption that time for color change of KI-starch paper is inversely proportional to the rate of NO_2 evolution. The value of the activation energy was determined to be 35 kcal/mol, which is very close to an anticipated value (37 kcal/mol) from Taliani test; data (Fig. 4). Thus the observed identity can provide a strong evidence for a conclusion

that the homolytic scission of RO-NO_2 bond and consequent evolution of NO_2 gas is the rate-determining step at low temperatures.

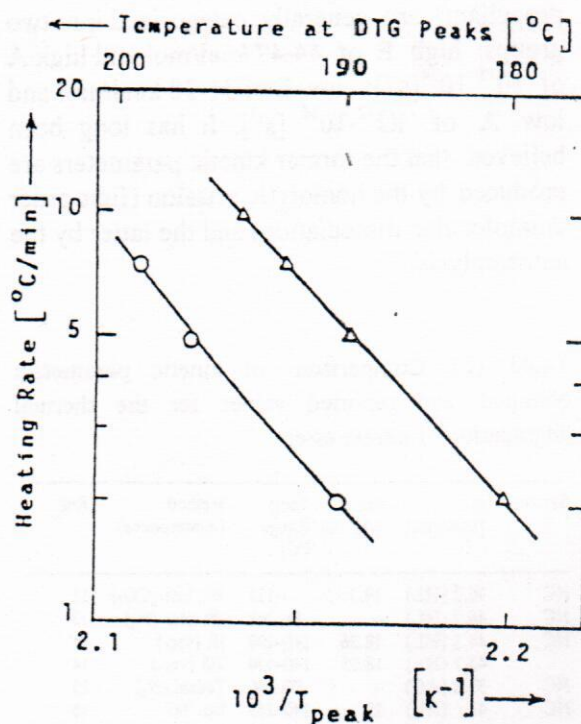


Fig. (6) Plot of log (heating rate) against reciprocal temperature of the DTG maximum of a double-base propellant obtained at a pressure of 0.16 atm. (Δ) $k=4.9 \times 10^{19} e^{(-46,000/RT)} \text{ s}^{-1}$ for NG decomposition (O) $k=6.5 \times 10^{19} e^{(-47,000/RT)} \text{ s}^{-1}$ for NC decomposition

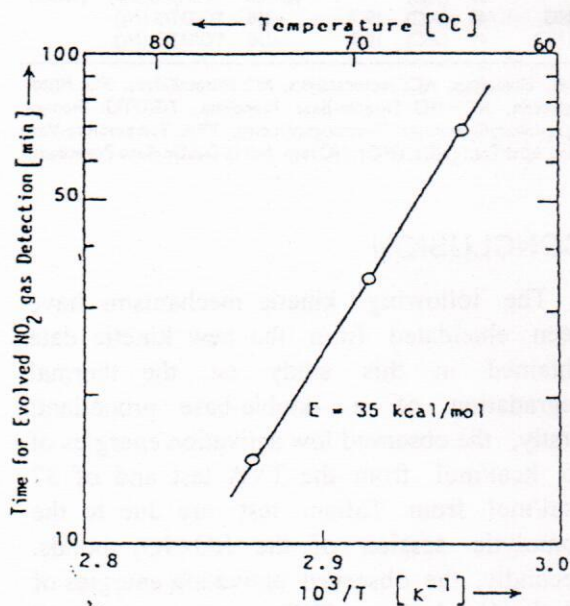


Fig. (7) Arrhenius plot of the TVA test results of a double-base propellant

Some comparison of kinetic parameters obtained in this study and those appeared in the literatures is appropriate. The published E and A for NC, NG, and NC+NG (double-base propellant) are generally categorized into two groups: high E of 44-47 kcal/mol and high A of 10^{18} - 10^{24} [s⁻¹]; low E of 31-38 kcal/mol and low A of 10^{12} - 10^{16} [s⁻¹]. It has long been believed that the former kinetic parameters are produced by the homolytic scission (first-order unimolecular dissociation) and the latter by the autocatalysis.

Table (2) Comparison of kinetic parameters obtained and reported values for the thermal degradation of nitrate esters

System	E [kcal/mol]	log A (A, 1/s)	Temp. Range [°C]	Method (Atmosphere)	Ref.
NC	46.2 (HL)	19.3	-135	Wt. loss (CO ₂)	12
NC	46.7 (HL)	-	84-162	Wt. loss (N ₂)	13
NC	44.3 (HL)	18.36	140-190	IR (vac.)	14
	43.7 (HL)	18.95	140-190	TG (vac.)	14
NC	37.6 (AC)	-	90-140	Taliani (N ₂)	15
NC	47 (HL)	19	140-165	Iso. TG	16
	31 (AC)	12	140-165	Iso. TG	16
NC	41.10	18.57	-250	DSC (N ₂)	17
NG	45.7 (HL)	23.5	120-135	Taliani (N ₂)	7
	34.3	15.1	120-135	Taliani (N ₂)	7
NG	46.9 (HL)	20.20	150-160	IR (Liq.)	18
	36.0 (AC)	15.51	150-160	IR (Gas)	18
NG	34.4 (HL)	14.4	90-160	IR (Liq.)	19
NC+NG	36.4	-	80-110	Calorimeter	2
NC+NG	45.3	18.88	-170	TG (Air)	20
	35.6	14.30	-212	DTA (Air)	20
NC+NG	49 (AC)	22.6	120-130	Taliani (N ₂)	This work
	37 (HL)	-	120-130	Taliani (N ₂)	(below)
	35 (HL)	-	60- 80	TVA (Air, Ar)	
NG	46 (AC)	19.7	-250	TG/DTG (N ₂)	
(NC)	47 (AC)	19.9	-250	TG/DTG (N ₂)	

HL: Homolysis, AC: Autocatalysis, NC: Nitrocellulose, NG: Nitroglycerin, NC+NG: Double-Base Propellant, TG/DTG: Thermogravimetry/Derivative Thermogravimetry, TVA: Temperature-Varied Abel Test; (NC), (NG): NC resp. NG in Double-Base Propellant.

CONCLUSION

The following kinetic mechanisms have been elucidated from the new kinetic data obtained in this study on the thermal degradation of a double-base propellant: firstly, the observed low activation energies of 35 kcal/mol from the TVA test and of 37 kcal/mol from Taliani test are due to the homolytic session of the RO-NO₂ bonds. Secondly, the observed activation energies of 49 kcal/mol from Taliani test and 46-47 kcal/mol from TG/DTG measurements are

originated from autocatalytic decomposition of NC and NG.

Figure 4 illustrates the domain of the two rate-determining reactions as a function of temperature and pressure of evolved gases.

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