

A kinetic model for the consumption of stabilizer in single base gun propellants

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A suitable kinetic model for the consumption of stabilizer (diphenylamine) in single base gun propellants was investigated and successfully verified. The model assumes that a reaction of shifting order can be applied for the consumption of diphenylamine in single base gun propellants. It was found that the experimental data were well evaluated by a first-order reaction at high concentrations of diphenylamine in the propellant, but by a zero-order reaction at low concentrations during the final phase of the propellant life time. The mechanism of diphenylamine depletion was discussed with relation to the model and the ageing behavior of the propellants. The kinetic parameters of this model, which permit the calculation of the time up to complete consumption of the diphenylamine, were determined. The results were compared with the kinetic data obtained by a widely accepted model, which combines formally reactions of first and zero order, designated as an “exponential and linear” model. All comparisons gave satisfactory agreement.

Keywords: single base gun propellants, stabilizer (diphenylamine) consumption, chemical stability, kinetic model.

INTRODUCTION

Single base (nitrocellulose-based) gun propellants degrade with time, producing oxides of nitrogen, which cause further self-catalytic, exothermic degradation even at moderate temperatures used for their storage (normally less than 40 °C or 50 °C). Since these gun propellants are not homogeneous, there is a possibility that in some regions the dissipation of the heat or gases evolved during decomposition may be prevented. The results would be a localized buildup of heat and gas pressure. In such propellant region the degradation rate would increase. If the temperature would rise to approximately 170 °C or 180 °C, self-ignition would occur. Therefore, these propellants must be stabilized with the substances, most frequently with diphenylamine (DPA), that chemically bind the evolved gases, in fact removing them from the matrix.

The knowledge of the stabilizer content and its consumption over a time-temperature range permits their safe storage and safe use time to be estimated. Several different approaches, which involve the artificial ageing of propellant samples at various

elevated temperatures and measuring the change in the “free” stabilizer content of the propellant and the formation of its consecutive nitrated products, have been used to obtain equations to predict the time for the consumption of a given percentage of the stabilizer and a temperature coefficient to allow an estimation of this time at the storage temperature.^{1–11} Some of the prediction methods were investigated for specific problems and it was found that they depend on the technique used to monitor the stabilizer. Other methods were intended to be a basic kinetic approach that could, at least in principle, be applied to any propellant chemical stability problem.

The objective of the present investigation was to find a suitable kinetic model for the consumption of diphenylamine in single base gun propellants and to determine the kinetic parameters, which enable the calculation of the times up to complete diphenylamine consumption over a time-temperature range.

DESCRIPTION OF THE MODEL

The reaction and diffusion processes causing stabilizer consumption in a propellant during its life time are very complex^{1,12,13} and a kinetic approach requires some simplifying assumptions.

It is assumed that a reaction of shifting order¹⁴ can be applied for the consumption of diphenylamine in single base gun propellants. Namely, when the diphenylamine concentration in the propellant is relatively high, the diphenylamine depletion approaches first-order kinetics, while during the final phase of the life time of the propellant, the diphenylamine depletion does not depend on its concentration, then the diphenylamine consumption inclines to a reaction of zero-order. This means that during this phase, diffusion processes of the decomposition products in a gun propellant are dominant. Further, it is accepted that the temperature dependence of the reaction rate constants follows Arrhenius type behavior.

In the adopted notation the rate equations describing the stabilizer consumption according to the accepted kinetic model are given by:

$$-\left(\frac{\partial c_{\text{DPA}}(t, T)}{\partial t}\right)_T = k_0(T) + k_1(T) c_{\text{DPA}}(t, T) \quad (1)$$

$$k_0(T) = Z_0 \exp\left(-\frac{E_{a,0}}{RT}\right) \quad (2)$$

$$k_1(T) = Z_1 \exp\left(-\frac{E_{a,1}}{RT}\right) \quad (3)$$

where c_{DPA} is the diphenylamine concentration in a propellant as a function of time t and temperature T , k_0 and k_1 are the reaction rate constants for the zero-order and first-order kinetics, respectively, Z_0 , Z_1 , $E_{a,0}$ and $E_{a,1}$ are the corresponding pre-exponential factors and the energies of activation in the Arrhenius equation, and R is the gas constant.

Integration of Eq. (1) yields:

$$c_{\text{DPA}}(t, T) = -\frac{k_0(T)}{k_1(T)} + \left[\frac{k_0(T)}{k_1(T)} + c_{\text{DPA}}(0, T) \right] \exp[-k_1(T)t] \quad (4)$$

Then, Eq. (4) describes the decrease in the diphenylamine content over a time-temperature range.

EXPERIMENTAL

The single base gun propellant NC-27, containing about 99 % nitrocellulose (NC) and 1 % diphenylamine, was subjected to artificial ageing at 100, 90, 80 and 60 °C for times necessary for the complete consumption of the stabilizer. These tests were run on 30 g samples using pyrex tubes (150 mm long by 25 mm diameter), capped with loosely ground glass stoppers. The entire tube was contained within the cavity of a heating block to ensure uniformity of heating and to avoid condensation at the top of the tube.

The stabilizer content in the aged propellant samples was measured by reverse-phase high performance liquid chromatography (HPLC).

The internal standard method was used for the quantitative determination of the sample components. The internal standard solution was prepared by dissolving 0.1 g of dimethyldiphenylurea, known as centralite II, in 50 ml of acetonitrile.

The propellant samples were ground (approximately to a size of 2 mm); 2 g of each were extracted for 48 h with 50 ml of dichloromethane. A 2 ml of this solution was pipetted into a 10 ml volumetric flask. The solvent was then evaporated, a 1 ml of the internal standard solution was added and the content of the flask was diluted to the mark with acetonitrile.

The concentration of the standard components (DPA, *N*-nitroso-DPA, 2-nitro-DPA and 4-nitro-DPA) in the 50 ml calibration mixture solution covered the ranges expected for the samples. A 2 ml sample of this solution was transferred into a 10 ml volumetric flask of and the dichloromethane was evaporated. A 1 ml of the internal standard solution was added and the content of the flask was diluted to the mark with acetonitrile.

A HPLC instrument LDC/Milton Roy 3000 was used. The variable wavelength UV-detector was set at a wavelength of 220 nm. The data were processed using a chromatography data system.

The column type was 150 mm × 4.6 mm Supelcosil LC-18-DB with a particle size of 3 μm. The operating temperature was maintained at 55 °C.

The mobile phase composition was acetonitrile/water, 40/60 (v/v) with a flow rate of 2 ml/min. The injection sample size was 5 μl.

RESULTS AND DISCUSSION

The HPLC analysis results obtained for aged propellant samples are presented in Figs. 1 and 2. All of these results formed the basis for the kinetic analysis, which was intended to verify the proposed kinetic model. The solid lines in these Figures were fitted according to Eq. (4). The model was assessed using the standard deviation (SD) of the least square fit procedure as the criterion. The results of these calculations and the corresponding reaction rate constants are presented in Table I.

As can be seen from Figs. 1 and 2, as well as from Table I, there is a good agreement between the corresponding measured and calculated concentrations of diphenylamine for the times up to its complete consumption. This fact confirms the

validity of the proposed kinetic model of the stabilizer consumption in single base gun propellants.

TABLE I. Reaction rate constants of the consumption of diphenylamine in the single base gun propellant NC-27

$T/^\circ\text{C}$	$k_0/(\text{mass \%}/\text{day})$	$k_1/(\text{l}/\text{day})$	$SD/\text{mass \%}$
100	0.1881	0.7526	0.02
90	0.0569	0.2275	0.04
80	0.0118	0.0784	0.03
60	0.0005	0.0051	0.01

The kinetic parameters of this reaction of shifting order, which were determined by the least square fit procedure according to Eqs. (2) and (3), are given in Table II.

The Arrhenius plots of the reaction rate constants for the diphenylamine consumption in the gun propellant NC-27 are presented in Fig. 3. The values lie very well on straight lines, as can be seen from the small confidence intervals of the activation energies and the pre-exponential factors, Table II.

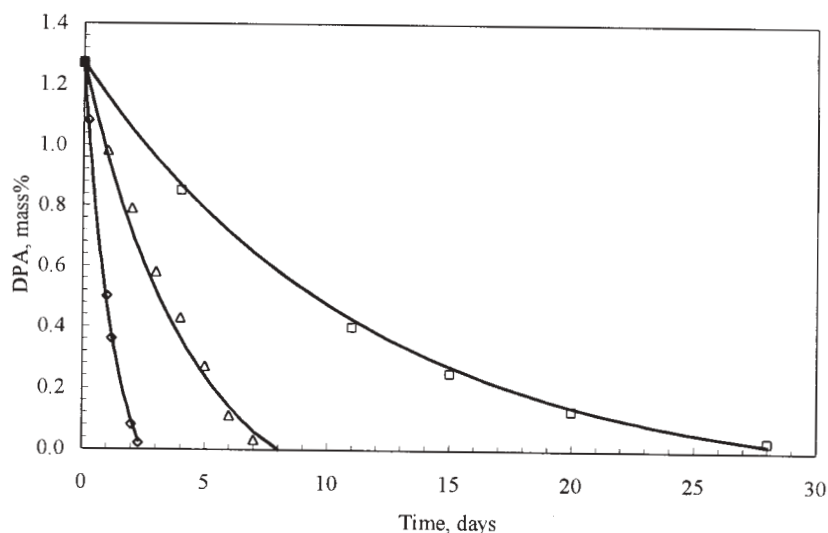


Fig. 1. Diphenylamine consumption in the single base gun propellant NC-27 – Description by a reaction of shifting order. □ – 80 °C; Δ – 90 °C; ◇ – 100 °C.

The values of the activation energies and the pre-exponential factors have been compared for the same type of gun propellants, with data obtained by a model which combines formally reactions of first and zero order, designated the “exponential and linear” model.^{9–11} The results are also given in Table II, and this comparison gives satisfactory agreement.

Diphenylamine chemically binds the evolved decomposition products of nitrocellulose and consecutive products with an increasing degree of nitration are formed. Hence, consecutive nitrated products of DPA, from the *N*-nitroso-DPA and the mono-nitro-deriva-

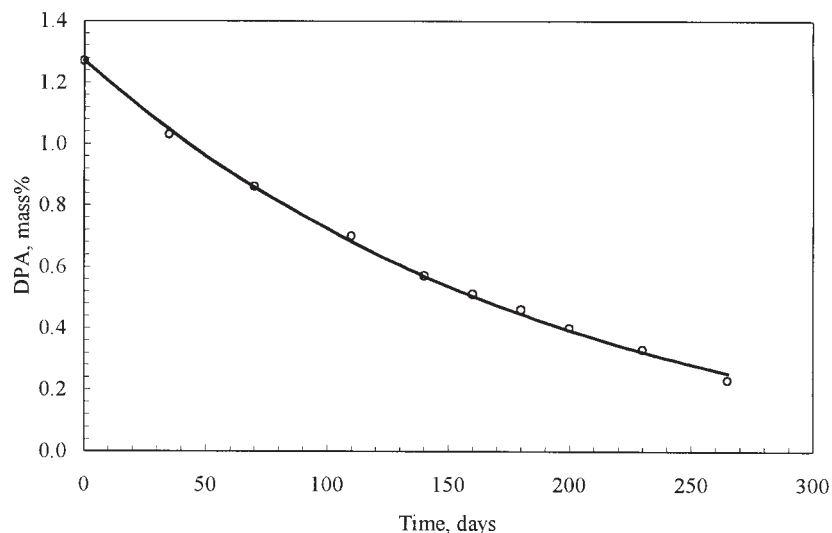


Fig. 2. Diphenylamine consumption in the single base gun propellant NC-27 – Description by a reaction of shifting order. 60 °C.

tives of DPA to the hexa-nitro-derivatives of DPA are formed with time. Some of them, *N*-nitroso-DPA and mono-nitro-derivatives of DPA, also have a stabilizing effect.¹³

TABLE II. Kinetic parameters of the consumption of diphenylamine in single base gun propellants over the temperature range from 60 °C to 100 °C

	NC-27	GP A5020 ^{9,11}
$E_{a,0}/\text{kJ mol}^{-1}$	154.0 ± 3.1	152.1 ± 8.6
$\ln Z_0/\text{mass \% s}^{-1}$	36.68 ± 0.79	36.23 ± 2.95
$Z_0/\text{mass \% s}^{-1}$	$8.48 \times 10^{+15}$	$5.446 \times 10^{+15}$
$E_{a,1}/\text{kJ mol}^{-1}$	128.3 ± 2.4	138.3 ± 3.7
$\ln Z_1/\text{s}^{-1}$	29.69 ± 0.60	33.36 ± 1.27
Z_1/s^{-1}	$7.82 \times 10^{+12}$	$3.078 \times 10^{+14}$

The results of the HPLC analysis, obtained for the propellant samples aged at 90 °C for times up to the complete consumption of the diphenylamine, are presented in Fig. 4.

As can be seen in Fig. 4, the concentrations of *N*-nitroso-DPA and mono-nitro-derivatives of DPA increase with increasing aging time. Since these DPA derivatives have an important stabilizing effect, they concurrently with the remaining DPA react with the NC decomposition products in a further step. When the DPA content becomes sufficiently small, the reactions of the DPA derivatives prevail, because the chemical accessibility of the unreacted DPA becomes a limiting factor. Then, diphenylamine depletion does not depend on its concentration, *i.e.*, the diphenylamine consumption tends to a reaction of zero-order or, during this phase, diffusion processes of the NC decomposition products in the gun propellant are predominant.

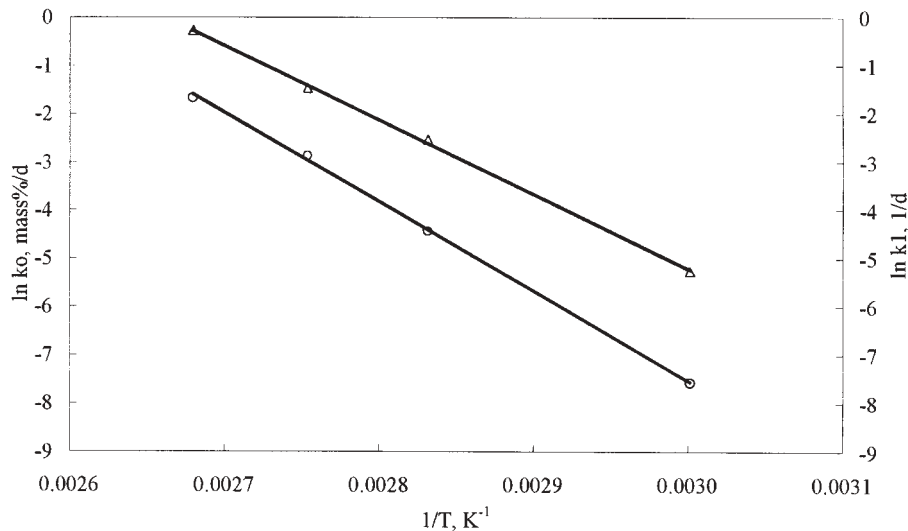


Fig. 3. Arrhenius plot of the reaction rate constants of the diphenylamine decrease in NC-27.
 $\diamond - \ln k_1$; $\circ - \ln k_0$.

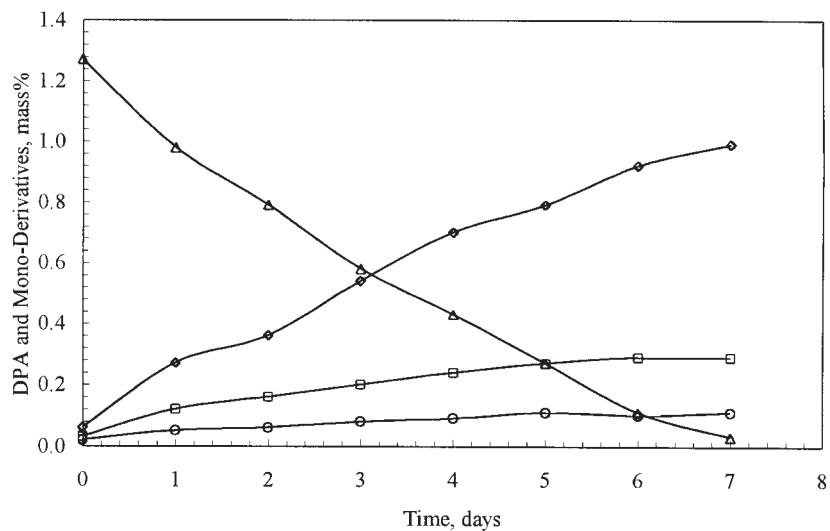


Fig. 4. Major stabilizer components in the single base propellant NC-27 as a function of time of aging at 90 °C. $\Delta - \text{DPA}$; $\diamond - N\text{-nitroso-DPA}$; $\square - 4\text{-nitro-DPA}$; $\circ - 2\text{-nitro-DPA}$.

CONCLUSION

A suitable kinetic model for the consumption of diphenylamine in single base gun propellants, which assumes that a reaction of shifting order can be applied for the diphenylamine depletion, was successfully verified. It was found that the experimental data were well evaluated by a first-order reaction at high concentrations of diphe-

nylamine in the propellant, but by a zero-order reaction of at low concentrations during the final phase of the propellant life times. The kinetic parameters of this model, which permit the calculation of the times up to complete consumption of diphenylamine, were determined. The results were compared with kinetic data obtained using a widely accepted model which combines formally the first- and zero-order reactions, designated as an "exponential and linear" model. All comparisons gave satisfactory agreement.

ИЗВОД

КИНЕТИЧКИ МОДЕЛ ПОТРОШЊЕ СТАБИЛИЗАТОРА У ЈЕДНОБАЗНИМ БАРУТИМА

ЉИЉАНА ЈЕЛИСАВАЦ и МИЛОШ ФИЛИПОВИЋ

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Истраживан је и успешно верификован кинетички модел потрошње стабилизатора (дифениламина) у једнобазним барутима. Овај модел претпоставља да се, за описивање потрошње дифениламина у једнобазним барутима, може применити реакција променљивог реда. Нађено је да се експериментални подаци веома добро процењују реакцијом првог реда при великим концентрацијама дифениламина у барутима и реакцијом нултог реда при малим концентрацијама током завршног периода употребљивости барута. Разматран је механизам трошења дифениламина у односу на модел и процес старења барута. Одређени су кинетички параметри овог модела који омогућава израчунавање времена потребног за потпуну потрошњу дифениламина. Резултати су поређени са кинетичким подацима добијеним по моделу који формално комбинује реакције првог и нултог реда, названим "експоненцијални и линеарни" модел, који је широко прихваћен. Сва поређења дала су задовољавајуће слагање.

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