

# Kinetic Analysis of Overlapping Multistep Thermal Decomposition Comprising Exothermic and Endothermic Processes: Thermolysis of Ammonium Dinitramide

Nikita V. Muravyev<sup>1,\*</sup>, Nobuyoshi Koga<sup>2</sup>, Dmitry B. Meerov<sup>1</sup>, and Alla N. Pivkina<sup>1</sup>

<sup>1</sup>Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., 119991 Moscow, Russia

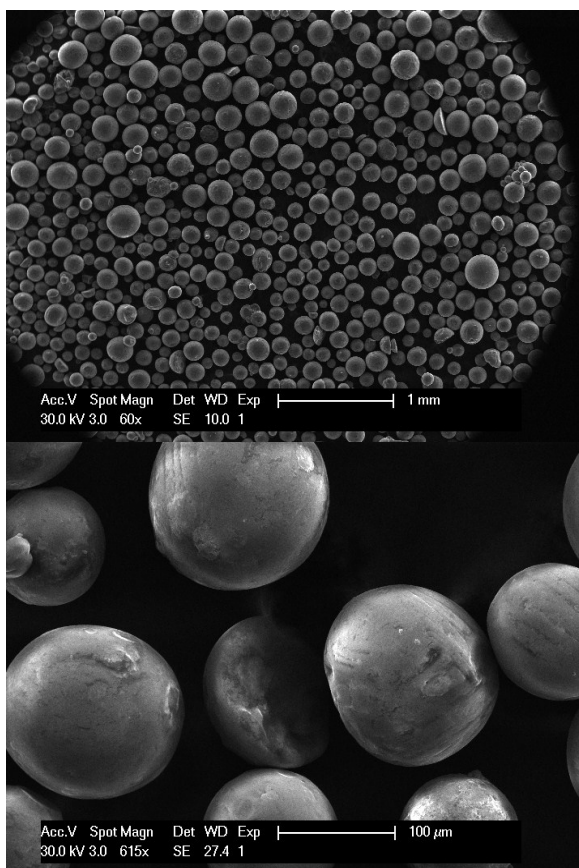
<sup>2</sup>Chemistry Laboratory, Department of Science Education, Graduate School of Education, Hiroshima University, 1-1-1 Kagamiyama, Higashi-Hiroshima 739-8524, Japan

\* Corresponding Author. Tel/Fax: Tel/Fax +74991378203. E-mail: [n.v.muravyev@ya.ru](mailto:n.v.muravyev@ya.ru).

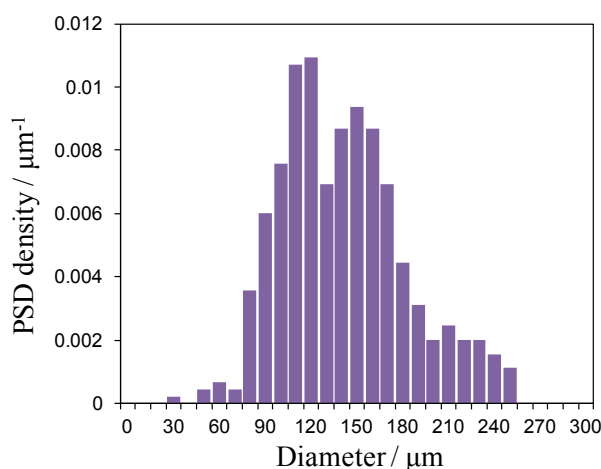
## Contents

S1. Sample morphology .....	1
S2. TG–DSC curves for kinetic calculation .....	2
S3. Interpretation of zero-order reaction model .....	2
S4. Simplified kinetic modeling using fixed model functions .....	2
S5. Kinetic compensation effect for the thermal decomposition of AN .....	2
References .....	2

## S1. Sample morphology

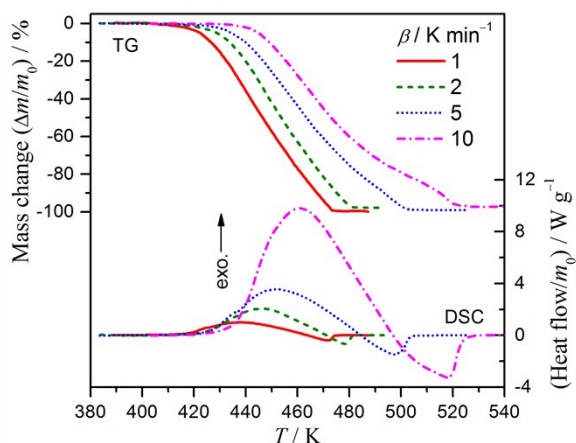


**Figure S1.** SEM images of an ADN sample (Helios NanoLab™ 660, FEI).



**Figure S2.** Size distribution of spherical ADN sample particles.

## S2. TG–DSC curves for kinetic calculation



**Figure S3.** TG–DSC curves for the thermal decomposition of ADN at different  $\beta$ .

## S3. Interpretation of zero-order reaction model

When evaporation is the predominant process for the mass-loss phenomena, the kinetic equation can be replaced by the thermodynamic equation based on the Langmuir equation:<sup>1</sup>

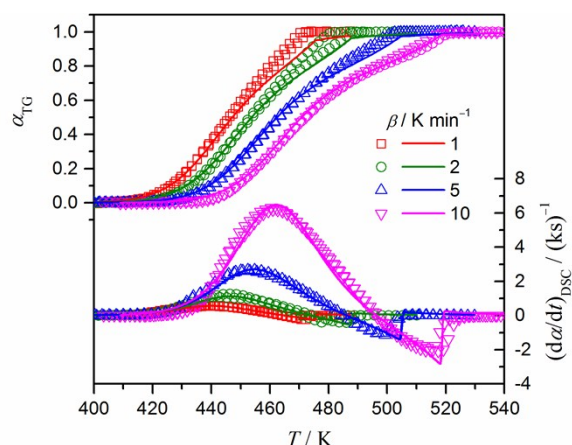
$$-\frac{dm}{dt} = \gamma PS \sqrt{\frac{M_g}{2\pi RT}} \quad (\text{S1})$$

where  $dm/dt$  is mass loss rate,  $R$  is the universal gas constant,  $\gamma$  is the vaporization coefficient,  $M_g$  is the molar mass of vapor,  $S$  is the surface area, and  $P$  is the vapor pressure. Combining Eq. (S1) with the Clausius-Clapeyron formula gives:

$$\begin{aligned} \frac{d\alpha}{dt} &= \exp(Z) \cdot \frac{\gamma S \sqrt{M_g}}{m_s \sqrt{2\pi RT}} \exp\left(-\frac{\Delta H_v}{RT}\right) \\ &= \frac{A^*}{m_s \sqrt{T}} \exp\left(-\frac{E_a^*}{RT}\right) \end{aligned} \quad (\text{S2})$$

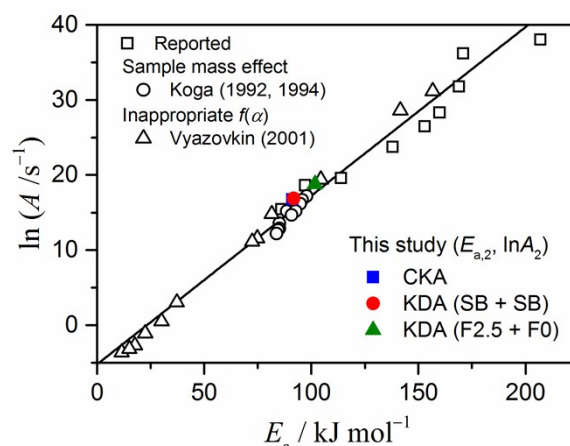
where  $Z$  is a constant,  $m_s$  is the sample mass, and  $\Delta H_v$  is the vaporization enthalpy. Comparing Eq. (S2) with the zero-order reaction type (F0) we can see the overall similarity and two significant differences: First, the effective pre-exponential factor should depend on the sample mass, which is in agreement with reported observations.<sup>2–4</sup> Second, the term  $1/T^{0.5}$  is added. The Langmuir equation was developed to describe vaporization in a vacuum, so to account for the non-vacuum conditions the diffusion in an inert gas is incorporated<sup>5</sup> and its temperature dependency is assumed as  $D = k_0 \cdot T^{3/2}$ ,<sup>6</sup> which leads to the temperature exponent in Eq. (S2) of  $1/2$  instead of  $-1/2$ . Nevertheless, this temperature dependence was found to be almost negligible in our calculations compared to the strong exponential term. Therefore, the zero-order kinetic model can be used as an empirical form of the kinetic equation of a vaporization process.

## S4. Simplified kinetic modeling using fixed model functions



**Figure S4.** The best fits of TG and DSC kinetic curves with Eqs. (12) and (13), respectively, obtained through combined KDA.

## S5. Kinetic compensation effect for the thermal decomposition of AN



**Figure S5.** Linear correlation among the literature values of  $(E_a, \ln A)$  reported for the thermal decomposition of AN, including those caused by sample mass effect<sup>2,4</sup> and inappropriate  $f(\alpha)$ ,<sup>7</sup> and correspondence of  $(E_{a,2}, \ln A_2)$  values determined in this study for the second reaction step to the regression line.

## References

- 1 I. Langmuir, *Phys. Rev.*, 1913, **2**, 329–342.
- 2 N. Koga and H. Tanaka, *Thermochim. Acta*, 1992, **209**, 127–134.
- 3 N. Koga and H. Tanaka, *J. Therm. Anal.*, 1993, **40**, 1173–1179.
- 4 N. Koga and H. Tanaka, *Thermochim. Acta*, 1994, **240**, 141–151.
- 5 I. Langmuir, *Phys. Rev.*, 1918, **12**, 368–370.
- 6 F. Barontini and V. Cozzani, *Thermochim. Acta*, 2007, **460**, 15–21.
- 7 S. Vyazovkin, J. S. Clawson and C. A. Wight, *Chem. Mater.*, 2001, **13**, 960–966.