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INFLUENCE OF PURITY ON THE THERMAL STABILITY OF SOLID ORGANIC COMPOUNDS

A. Książczak[*]*, Teresa Książczak and T. Zielenkiewicz*

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Abstract

DSC method was used to study thermal stability of nitrocompounds. It was assumed the model to estimate stability of solid phase in which perfect solid phase is totally stable and amorphous-liquid domains connected with impurities decompose according to the kinetic model determined for the liquid phase above the melting point. The influence of sample purity on relative stability, which is k_l/k_s – ratio of decomposition rate constants in liquid and solid phase, at temperature 20 K below the melting point was predicted. The increase of liquid domains in solid phase causes decrease of k_l/k_s ratio (relative stability) at chosen temperature.

Keywords: diphase model, DSC, nitrocompounds, purity, thermal decomposition

Introduction

Properties of biologically active or pharmaceutical compounds as well as compounds used in energetic materials depend strongly on their purity, which can change with time. One of the elements of purity changes is thermal decomposition. Examinations of thermal stability in the solid phase are very time consuming. Thermal decomposition processes run much slower in the solid phase than in the liquid phase. The thermal effects of solid phase decomposition are small per time unit and hard to examine by thermal analysis methods. DSC and TG/DTA methods are frequently used to the investigation of energetic materials [1, 2]. Non-isothermal DTA and DSC measurements make it possible to obtain thermal stability in the liquid phase when the rate of the decomposition reaction is higher and when it is connected with high temperatures of the decomposition process. That is why there is much more information available about the thermal decomposition of organic compounds in the liquid phase than in the solid phase. Methods of predicting solid phase kinetic parameters (k_s) using liquid phase kinetic parameters (k_l), which are easier to obtain, need to be worked out.

Bawn [3] has presented a method of k_l/k_s ratio prediction at specified temperatures. This method is based on an assumption that the temperature dependence of the decomposition rate constant in solid phase (k_s) and liquid phase (k_l) can be described

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[*] Author for correspondence: E-mail: andrzks@ch.pw.edu.pl

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by the Arrhenius equation. Preexponential parameters are equal for both phases (A_l=A_s). Thus, we can formulate the k_l/k_s ratio as follows:

$$\ln\left(\frac{k_l}{k_s}\right)=\ln\left(\frac{A_l}{A_s}\right)+\frac{(E_s-E_l)}{RT}\approx\frac{(E_s-E_l)}{RT} \tag{1}$$

where E_s and E_l are the activation energies for solid and liquid phase, respectively. The difference between these energies is equal to melting heat. It lets us predict the k_l/k_s ratio in a specified temperature.

The aim of this work is to propose a method of estimating the k_l/k_s ratio using a diphase model of substances below their melting temperatures and to verify this method by applying it in the examination of chosen substances.

Diphase model of the solid substance decomposition

In order to estimate the kinetics of solid substance decomposition using liquid phase decomposition kinetics, it must be assumed that:

- the solid substance consists of perfectly ordered crystal domains and liquid domains,
- the decomposition of the solid substance is connected mainly with liquid domains decomposition.

The stability of the solid substance depends on the amount of liquid phase that is included in this substance. The presence of the liquid phase is connected with impurities in the examined substance. The liquid–crystal equilibrium of the system consisting of this substance and its impurities decides about the liquid phase content. If we want to predict this equilibrium we should know the constitution of the impurities and their physicochemical properties like: melting temperature, melting enthalpy and the activity coefficient of each component. In most cases the composition of impurities, which consist of a few or dozens of substances, is not known. For this very reason we should make an assumption to predict the liquid–crystal equilibrium. Namely, that the impurities and the examined substance form an ideal solution – ingredients are soluble in the liquid phase and insoluble in the solid phase (eutectic phase diagram). For small amounts of impurities (x^0<0.03) the liquid–crystal equilibrium can be described approximately by the van't Hoff equation:

$$T_m=T_m^0-\frac{R(T^0)^2}{\Delta H_m}x^0\frac{1}{F} \tag{2}$$

where T_m – is the equilibrium temperature (liquidus temperature), T_m^0– the melting temperature of the absolutely pure substance, R – gas constant, ΔH_m – the melting enthalpy, x^0 – summary molar fraction of impurities, F – the melted fraction of a sample which is the ratio of the liquid mass and the total mass.

Basing on the DSC curves it is difficult to estimate the temperature of the melting process beginning. The observed deviation in temperature from the base line on the DSC curve (T_{on}) is treated as the temperature at which melting begins. In this cause, the melted fraction (F) is equal to the heat ratio of the sample's melting (ΔH_t) from (T_{on}) to the equilibrium temperature (T_m) and total heat connected with the melting process (ΔH_m).

$$F = \frac{\Delta H_t}{\Delta H_m} \tag{3}$$

In most cases at (T_{on}) part of the investigated sample is in the liquid phase (w). For this very reasons, the melting fraction F can be described with the following equation:

$$F = \frac{\Delta H_t + w}{\Delta H_m + w} \tag{4}$$

In practice, only by applying the correction (w) in Eq. (4) can a straight line plot of temperature (T_m), *vs*. a reciprocal of the melted fraction ($1/F$) be obtained [4].

The value of the correction (w) increases after successive melting processes in the same sample of the unstable substance [5]. This means the increase of liquid domains is connected with impurities, which form as the result of thermal decomposition.

From a practical point of view it is interesting to specify the influence of impurities on decomposition kinetics for small conversion degrees ($\alpha \ll 1$) below the melting temperature. It was assumed that the decomposition rate of the liquid existing in the solid under consideration is equal to the initial rate in the supercooled liquid phase at the same temperature and that the volume change of melting is small. For zero order kinetic model ($\alpha \ll 1$) the k_l/k_s ratio for the diphase model of organic solid compounds is equal to [3]:

$$k_l/k_s = 1/F = n_{ll}/n_{ls} \tag{5}$$

where k_l and k_s are the rate constant of supercooled liquid and solid phase, respectively, n_{ll} and n_{ls} are the number of moles of supercooled liquid and the number of moles of liquids in the solid compounds for the same volume. It is worth emphasizing that parameter F possesses a similar meaning as a parameter β (fraction of molecules on the surface of the solid) introduced by Garner [3].

Experimental

N,2,4,6-tetranitro-N-metyloaniline (TET) and 2,4,6-trinitrotoluene (TNT) were prepared and purified in the Department of Analytical Chemistry of the Institute of Organic Industrial Chemistry. Their purity was determined by the cryometric method and was equal 99.8 and 99.6 mol%, respectively.

Samples with a mass of approx. 10 mg were closed in aluminium pans under a reduced pressure of about 1.3 kPa. Samples were then carefully decomposed during DSC measurements with a heating rate of 2 K min^{-1} to the same final temperature (T_f). The mole fraction of impurities was determined by the cryometric method [6]. This way solids with different degrees of purity were obtained from the same substance.

Results and discussion

Figure 1 shows the DSC curves for consecutive melting of TET performed on the same sample. The final temperature was T_f=417.6 K for all measurements. The melting curves for consecutive melting processes are shifted in the direction of lower temperatures. This shift is due to the thermal decomposition process.

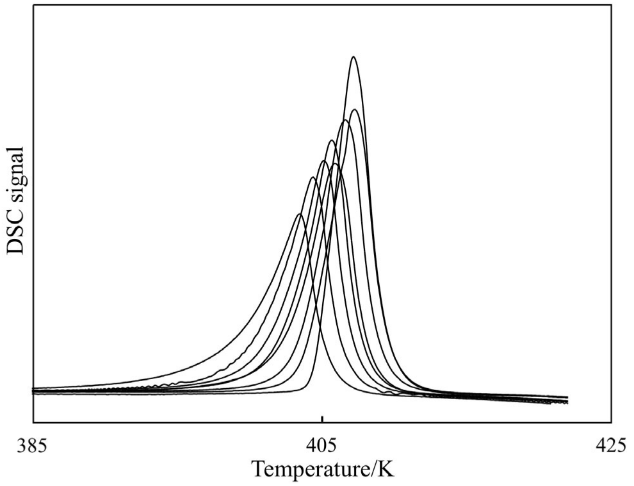

Fig. 1 Comparison of the consecutive DSC curves for TET melting performed on the same sample. The measurements were carried out with the heating rate of β=2 K min^{-1} to the final temperature of 417.6 K

Similar measurements were carried out on TNT. Figure 2 shows the DSC curves of the consecutive melting processes for TNT with the same final temperature T_f=520 K. Measurements of the melting processes were used to obtain parameter (w) and impurities production in the consecutive thermal decomposition processes.

Figure 3 shows a typical plot of temperature (T_m) *vs*. reciprocal of TNT melted fraction $1/F$ calculated by using Eq. (3) (circles). In this case the experimental results are not described by the van't Hoff expression (Eq. (2)). The straight line in practice has led to the empirical correction (w) for obtaining the best fit of the straight line to the van't Hoff curves. The introduction of the correction 'w' by Eq. (4) gives a linear dependence (squares). This linearization method was used to obtain parameter (w) as the correction on the amount of liquid (w) at temperature T_{on} for each melting process performed on the same sample.

Figure 4 shows the dependence of the melting enthalpy (ΔH_m) obtained directly from DSC measurements (points •) and the corrected melting enthalpy (ΔH_{mc}) (points ♦) calculated according to the following equation,

$$\Delta H_{mc}=\Delta H_m+w \qquad (6)$$

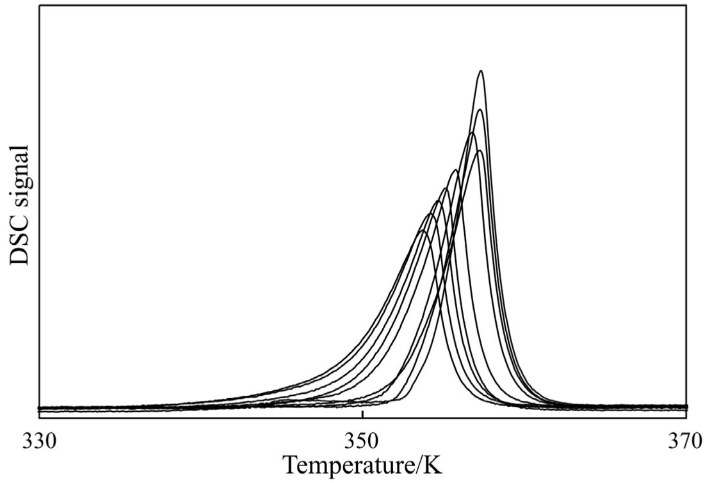

Fig. 2 DSC curves of the TNT melting process for consecutive measurements performed on the same sample. Measurements were carried out with the heating rate of β=2 K min^{-1} to the final temperature of 520 K

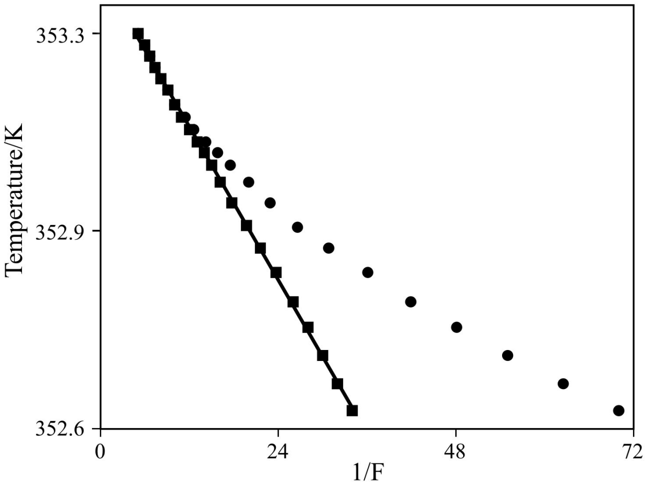

Fig. 3 The van't Hoff plot for TNT before linearization (circles) and afterwards (squares)

upon the number of measurements made on the same sample (No.). The melting enthalpy (ΔH_m) decreases in following measurements, which shows an increase of the liquid content in temperature T_{on} in consecutive melting processes. This means that in temperatures lower than T_{on} the liquid content increases and causes a decrease in stability. The small decrease of values of the corrected melting enthalpy (ΔH_{mc}) is due to the consumption of TNT molecules by the thermal decomposition process. This result shows that correction (w) obtained by linearization possesses the physico-

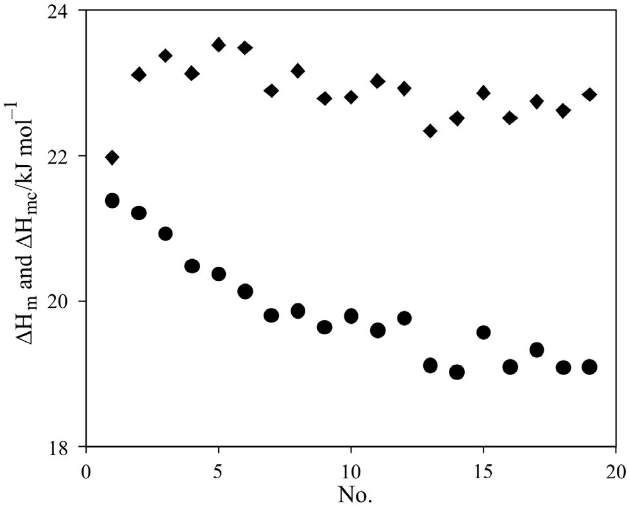

Fig. 4 The dependence of melting enthalpy (ΔH_m) obtained directly from DSC measurements (points)● and corrected melting enthalpy (ΔH_{mc}) (points)◆ on the number of measurements made on the same sample (No.)

chemical meaning attributed to it (w) and can be used to predict the k_l/k_s ratio below the T_{on} temperature using Eqs (2) and (5).

Figure 5 shows the dependence of the k_l/k_s ratio on the impurity content at the temperature of 20 K below the melting temperature of TNT. These values were obtained from DSC measurements of the melting process and Eqs (2), (4) and (5). Small changes in purity cause large changes of the k_l/k_s ratio for high purity TNT.

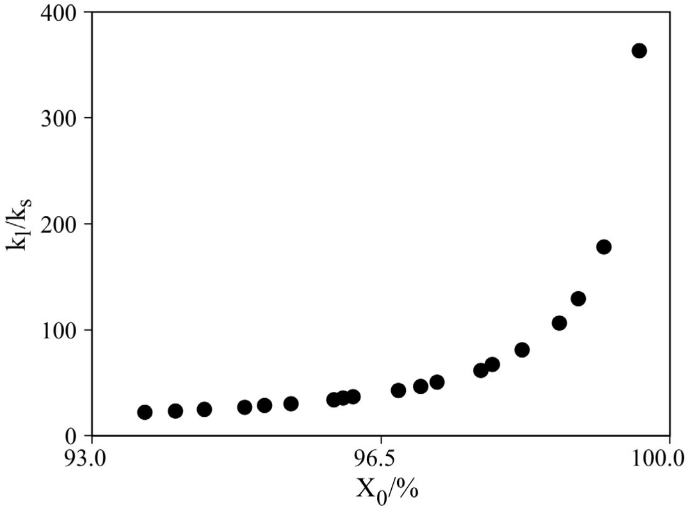

Fig. 5 The dependence of the k_l/k_s ratio on TNT purity calculated from DSC measurements

Figure 6 shows the dependence of the k_l/k_s ratio on the reciprocal of impurity content (x^0) at the temperature of 20 K below the melting temperature of TET. The points represent the values of the k_l/k_s ratio calculated from DSC measurements of the melting process and Eqs (2), (4). The line on the graph presents the values of the k_l/k_s ratio predicted from Eq. (2), the melting enthalpy and the melting temperature of TET. Points oscillate near the line. This suggests that deviations are connected with experimental errors. The k_l/k_s ratios predicted by two independent methods are consistent.

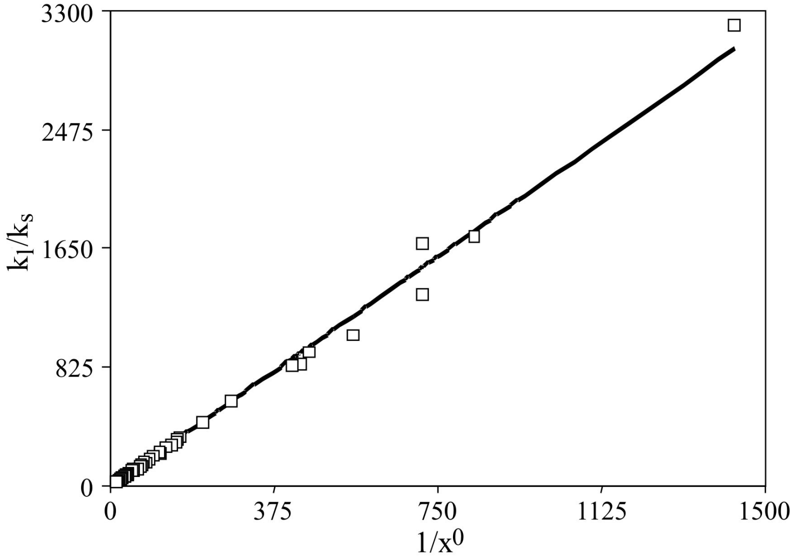

Fig. 6 Dependence of predicted k_l/k_s ratio on the reciprocal of impurities content $1/x^0$ at the temperature of 20 K below the TET melting temperature, points – the k_l/k_s ratio calculated from DSC measurements, the line – values calculated based on Eq. (2) and the physicochemical properties of TET

Figure 7 shows the dependence of the k_l/k_s ratio calculated at 293 and 393 K upon the melting temperature of the pure substance (T^0) for the same purity $(1–x^0)$=99.9 mol% and melting enthalpy ΔH_m=30 kJ mol^{-1}. This ratio increases with an increase in the melting temperature. This in turn shows that relative stability (k_l/k_s) for different substances with the same purity and melting enthalpy increases with the increase of the melting temperature.

The proposed model was checked by estimating purity which would justify the experimentally determined value of the k_l/k_s ratio (in the chosen temperature using kinetic data from literature). The k_l/k_s ratio values for TET are collected in Table 1. They were obtained from experimentally estimated kinetic parameters taken from literature [3] and [7–9] and purities needed to justify these values from proposed diphase model. In the last line the estimated purity is high and the probability of obtaining such a result in laboratory conditions is very low. The rest of the estimated purity values 0.22 and

Table 1 The k_l/k_s ratio of TET at 20 K below its melting temperature and purity estimated using Eqs (2) and (5)

k_l/k_s	x^0 (obl)/100 mol%	[Ref.]
126	0.220	[7]
46	0.770	[3]
29920	0.009	[8, 9]

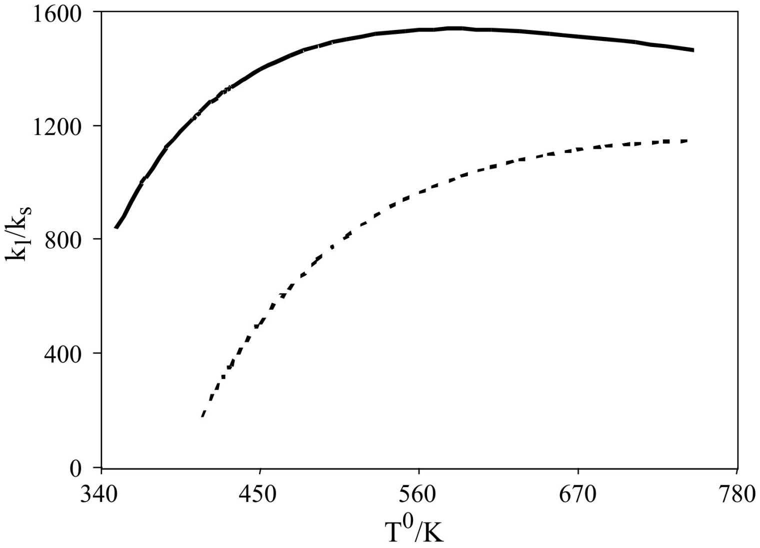

Fig. 7 Dependence of the k_l/k_s ratio calculated at 293 K (full line) and 393 K (broken line) upon the melting temperature for the same purity $(1-x^0)$=99.9 mol% and melting enthalpy ΔH_m=30 kJ mol^{-1}

0.77 mol% are more probable. The very high estimated purity suggests that kinetic parameters used in the calculations are burdened with high uncertainty.

Table 2 presents the kinetic parameters for the solid and liquid phase of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). The rate constants at 20 K below the melting temperature (457 K) are collected in the sixth column. The predicted rate constant for the solid phase in the last line differs significantly from others.

Table 3 shows k_l/k_s ratios calculated using rate constants for liquid phase with corresponding number (No.), attributed to them in Table 2. Only values from the seventh line in Table 2, which were used to estimate the k_l/k_s ratio, indicate that RDX with improbably high purity, higher than 99.98 mol%, was used. This suggests that values from the last column [15, 16] are very improbable. Subscript of the k_l/k_s ratio and No. in the first column of Table 3 mean the number (No.) attributed to the rate constants in the Table 2.

Table 2 Kinetic parameters of RDX and decomposition rate constants at 457 K (20 K below the melting temperature) determined by different methods

No.	Method	Phase	E_a/kJ mol^{-1}	log$A$	k_{457}/s$^{-1}\cdot 10^5$	[Ref.]
1	Manom	liquid	198.9	18.5	5.822	[7]
2	DSC	liquid	197.1	18.3	5.900	[8]
3	TG	liquid	200.4	18.7	6.218	[9]
4	DSC	liquid	211.8	19.6	2.458	[10]
5	SMM	solid	213.5	18.6	0.157	[11]
6	SMM	solid	217.6	19.1	0.169	[12]
7	SMM	solid	167	11.2	0.001	[13, 14]

Table 3 k_l/k_s ratios of RDX calculated based on data from Table 2 and purities calculated from Eqs (2) and (5)

No.	$k_l/k_{s(5)}$	$x^0_{(5)}$/mol%	$k_l/k_{s(6)}$	$x^0_{(6)}$/mol%	$k_l/k_{s(7)}$	$x^0_{(7)}$/mol%
1	37	1.0	34	1.1	4507	0.0084
2	38	1.0	35	1.1	4567	0.0083
3	40	1.0	37	1.0	4813	0.0079
4	16	2.4	15	2.6	1903	0.0199

Conclusions

Impurities cause the presence of a liquid domain in solid organic compounds. The decomposition of the solid phase can be considered as liquid domains decomposition which are present next to high stable crystals (diphase solid substance model). The proposed method lets us predict relative stability k_l/k_s using pure substance properties (T^0_m, ΔH_m) and purity (x^0). The value of the thermal decomposition rate constant of the solid depends strongly on the purity of the studied compounds.

In the case of substances with the same purity and thermal stability of liquid phase at chosen temperatures – the substance with a higher melting temperature is more stable. Whereas, in the case of substances with the same melting temperatures and thermal stability of liquid phase – the substance with a higher purity is more stable.

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