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The search for kinetic reference materials for adiabatic and differential scanning calorimetry

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Abstract No reference materials are currently available to study thermoanalytical kinetic methods, apparatus, or software. The ASTM International Committee E27 on Hazard Potential of Chemicals seeks to identify possible calorimetric reference materials for evaluating kinetic parameters, including activation energy (*E*), log pre-exponential factor (log *Z*), and reaction orders (*m* and *n*), as well as reaction enthalpy (*H*). Six candidate materials are examined including di-tertiary-butyl peroxide (DTBP), trityl azide, azobenzene, azobisisobutyronitrile (ABIN), cumene hydroperoxide (CHP), and phenytetrazolthiol. No single material appears to meet all needs. The merits and applicability of each candidate are discussed and recommended kinetic reference values are presented.

Keywords Kinetics · Reference materials · Calorimetery · DTBP · AIBN · Trityl azide · Phenyltetrazolthiol

Introduction

Quality initiatives, such as ISO16949, require the calibration of apparatus using certified and traceable reference materials [1]. In calorimetry, standard methods and reference materials exist for the calibration of each signal of time, temperature, and enthalpy [2–4]. The situation is less clear when it comes to calorimetric applications that involve more complex mathematical treatments such as the study of kinetics.

There are several kinetic methods available for thermal analysis users including the Ozawa–Flynn–Wall [5–7], Borchardt and Daniels [8, 9], Sestak Berggren [10–12], and Vyazovkin [13] methods for which commercially available software exists. Each of these methods has its own application area and none of these methods is applicable to all the situations.

Kinetics is the study of the dependence of a chemical reaction on time and temperature. Kinetic methods provide tools for estimating performance in experimental (temperature or time) regions that are difficult to reach [14]. For example, engineers may be required to design for lifetimes on the order of 40 years. Kinetic models help to estimate performance into this far-distant future.

The general kinetic equation, known as the Sestak–Berggren or autocatalytic equation [10–12] has the form of

$$\mathrm{d}\alpha/\mathrm{d}t = \alpha^m (1-\alpha)^n Z \exp(-E/RT) \quad (1)$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of reaction, α the fraction left to reaction (1 to 0), Z the pre-exponential factor (in s^{-1}), exp is the natural logarithm base e raised to the power of (·), R the molar gas constant (=8.32 $\mathrm{JK}^{-1}\ \mathrm{mol}^{-1}$), E is the activation energy (in $\mathrm{J\ mol}^{-1}$), T the absolute temperature (in K), and m and n are reaction orders (dimensionless). Equation 1 reduces to the more familiar *n*th order general rate equation when m equals zero.

$$\mathrm{d}\alpha/\mathrm{d}t = (1-\alpha)^n Z \exp(-E/RT) \quad (2)$$

The study of kinetics, then, involves the determination of the values for activation energy (*E*), ln or log (pre-exponential factor) (log *Z*), and reaction orders (*m* and *n*) for a particular reaction. Of these, activation energy is the most important, as it predicts how the reaction rate will change with temperature and is sometimes determined alone, as in "model free" kinetic methods. Although not a specific kinetic parameter, the enthalpy of reaction (ΔH) is often additionally determined in kinetics studies.

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In practice, the four kinetic parameters (E, log Z, m, and n) are simultaneously determined for a set of data using multiple linear regression and the logarithmic form of Eq. 1 shown in Eq. 3.

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = m\ln(\alpha) + n\ln(1-\alpha) + \ln(Z) - E/RT \tag{3}$$

Because the four kinetic parameters are determined simultaneously, a change in one determined value will affect the values determined for the other three. In particular, E and log (Z) are known to be related to each other by the kinetic compensation effect [15, 16]. The difficulty of determining four parameters simultaneously to high precisions is reduced by simplifying the number of determined parameters, usually by fixing values for m and n (this is called assigning a kinetic model). Experience shows that in thermal analysis, it is often reasonable to assume first-order reactions (i.e., $m = 0$ and $n = 1$).

To validate kinetic methods, the International Conference on Thermal Analysis and Calorimetry (ICTAC) has taken a mathematical approach. They chose to develop several sets of synthetic data modeled upon real systems [17]. One such example is the "standard" experimental data (free from noise and ideally suited for data analysis) for the single-step decomposition of calcium carbonate. ICTAC used this synthetic data to test several kinetic methods [17]. The synthetic calcium carbonate decomposition showed a 16% relative standard deviation for activation energy, a 25% relative standard deviation for log (pre-exponential factor), and a 39% relative standard deviation for the reaction order. These values provide inter-method reliability as the same data sets are examined by several kinetic methods.

The imprecision of kinetic values within a method is demonstrated in interlaboratory tests where the same material is treated by different laboratories using the same procedure. Interlaboratory tests show the between-laboratory reproducibility to be about 10% for activation energy and log (pre-exponential factor) and about 22% or the reaction order [12].

This inter-method reliability and intra-method reproducibility argue for a real world test material to be available for validation of methods, instruments, and software. That is, a kinetic reference material is needed.

Search for kinetic reference materials

The modern search for kinetic reference materials began in the 1970s when Allan Duswalt and Jimmy McCarty of Hercules Research looked for a suitable reference material during their development of ASTM International standard E 698, a variable heating rate method that assumes a first-order reaction [18]. The decomposition of peroxides (R–O–O–R) and azides (R–N=N=N) was suggested as likely candidates as they generally are clean, first-order reactions.

The selection of acceptable reference materials depends upon a series of requirements. The first of these is that the material must be readily available in consistent, high (or at least known) purity. In practice, this means that the material should be commercially available. Second, the desired measurement parameters must be well established with known and acceptable uncertainties. The reference material must be stable over time (so that it will be available for years once characterized) and be non-toxic and safe for transportation. Finally, it is desirable that the material be universally applicable to all methods, software, and instruments. The challenge with candidate kinetic reference materials is that no single material has been found to satisfy all of these criteria. We are faced, then, with reducing our expectations.

Di-*t*-Butyl peroxide (DTBP) (CAS: 110-05-4)

Di-t-butyl peroxide has been more studied as a kinetic reference than any other material. The decomposition is a smooth, continuous, and well-behaved first-order reaction. More than 30 kinetic studies are available in the literature (see Table 1). These studies provide sound kinetic values with precision for activation energy, enthalpy of reaction, pre-exponential factor, and reaction order. DTBP is commercially available in high concentration[1,2,3,4] and is non-toxic with an LD_{50} (oral, rat) of 25,000 mg/kg (see footnote 3). Lethal dose for 50% of the population of rats by oral intake is 25,000 mg/kg of body weight. Materials with $\mathrm{LD}_{50} < 500$ mg/kg are considered to be "toxic" [19]. These desirable qualities are mitigated by its boiling temperature of 110 °C making it unsuitable for the variable heating rate DSC methods.

Trityl azide (CAS: 14309-25-2)

Trityl azide (also known as azidotriphenylmethane) is a solid material with a melting temperature about 61 °C that possesses a clean "text book" shaped decomposition profile suitable for the Borchardt and Daniel method. It has been used in a number of interlaboratory tests for kinetic methods [20, 21]. Outside of the interlaboratory tests, there is little kinetic parameter information in the literature. Moreover, its toxicity is unknown. An inorganic azide

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[1] Arcos Organics, Fair Lawn, NJ.

[2] Pfalz & Bauer, Waterbury, CT.

[3] Sigma-Aldrich, Milwaukee, WI.

[4] TCI, Portland, OR.

Table 1 Kinetic parameters for di-*t*-butyl peroxide

E/kJ mol^{-1}	Log *A*/s^{-1}	Enthalpy/kJ g^{-1}	Order	Conditions	Reference
148	16.15				[28]
163	16.45			Gas phase	[29]
154	15.11			DSC, mineral oil	[30]
158	16.36			ARC, mineral oil, or toluene	[30]
122.1 ± 2.8	11.51 ± 0.33	1.19 ± 0.02		DSC, 725 psi	[31]
136	12.87			0.1 M in diesel fuel	[32]
148	14.87			Neat	[33]
140	13.74			Neat	[34]
159.2 ± 9.9	16.3 ± 1.2			30–60% in toluene	[35]
146.7 ± 7.0	15.0 ± 0 .9			30–60% in benzene	[35]
158.5	16.1	1.31		ARC	[36]
145.5	15.1	1.82		DSC	[36]
147.3 ± 0.4	15.68 ± 0.44	1.29	0.925 ± 0.088	ARC	[37]
158.2	16.15	1.19			[38]
		1.335			[39]
159				In *t*-butyl benzene	[40]
151				In toluene	[41]
142				In vapor phase	[41]
163				In vapor phase	[42, 43]
157				In *i*-propyl-benzene	[42, 43]
159				In *t*-butylbenzene	[42, 43]
155				In *t*-butylamine	[42, 43]
159.7 ± 0.58	15.94 ± 0.07			In vapor phase	[44]
157.7 ± 0.63	15.71 ± 0.08				[45, 46]
138.4 ± 2.5	13.16 ± 0.31				[41]
146.7 ± 6.7	14.04 ± 0.83				[47]
161.3 ± 3.1	16.30 ± 0.39				[48]
164.5 ± 1.0	16.63 ± 0.24			In diethylketone	[49]
158.4 ± 1.2	15.82 ± 0.18				[50]
152.6 ± 1.5	15.33 ± 0.13			In vapor phase	[51]
160.1 ± 1.3	16.07 ± 0.14				[52]
158.1 ± 0.25	15.80 ± 0.03		1.0	Gas phase “best” literature average	[50]
154.7	15.634			Solution	[53]
163.03	15.95^{-}				[54]
157.3 ± 2.1	15.94 ± 0.34		1.0	15% in toluene	[55]
		1.25 ± 0.04			[56]
152.0 ± 6.1			(1.0)	20% in toluene	[57]
158.2 ± 4.9	16.06 ± 0.59		1.0 ± 0.05	20% in toluene and benzene	[24]
161		0.557			[58]

Values in *parentheses* are assumed

analog, sodium azide, is quite toxic with an LD_{50} (oral, rat) = 27 mg/kg and is sometimes used as a biocide. Organic azides are considered less toxic but these materials must be treated with great caution. Table 2 provides the literature-supplied kinetic values for trityl azide. Trityl azide is commercially available (see footnote 2).

Azobisisobutyronitrile (AIBN) (CAS: 78-67-1)

Azobisisobutyronitrile, commercially available as DuPont’s VAZO® 64, is another candidate. It is a well-known blowing agent and polymerization initiator. It is a solid with a melting temperature of 102 °C making it a

Table 2 Kinetic parameters for trityl azide

E/kJ/mol	Log (Z)/s^{-1}	H/J g^{-1}	Order	Conditions	Reference
145 ± 11	17.0 ± 1.7		(1.00)	ASTM E698	[20]
165.1 ± 17	19.0 ± 2.0		1.32 ± 0.30	ASTM E2041	[21]
		724 ± 42		ASTM E537	[72, 73]

Values in *parentheses* are assumed

Table 3 Kinetic parameters for azobisisobutyonitrile (AIBN)

E/kJ mol^{-1}	Log (Z)/s^{-1}	H/J g^{-1}	Order	Conditions	Reference
182				4% in toluene	[59]
129	15.20		(1.00)		[60]
121.3 ± 9.2	14.42 ± 1.3		1.02		[61]
117.9 ± 2.7	14.11 ± 1.0		1.03		[61]
99.7	13.24		(1.00)	ASTM E698	[61]
128.5 ± 8.4	15.12 ± 1.1	1238 ± 78	(1.00)		[62]

Values in *parentheses* are assumed

Table 4 Kinetic parameters for azobenzene

E/kJ mol^{-1}	Log A/s^{-1}	Enthalpy/J g^{-1}	Order	Conditions	Reference
103.4 ± 1.6	12.2 ± 0.25	264.5 ± 1.6			[63]
103.5 ± 1					[22]
102.5 ± 0.8	11.98 ± 0.1	253.7 ± 5.4		Melt	[23]

Values in *parentheses* are assumed

good candidate for reference material for DSC, and accelerating rate calorimeters where it is commonly tested as a 10 to 15% solution in dichloromethane. Some half dozen kinetic studies provide reasonable kinetic parameters (see Table 3). Its one challenge is its toxicity with an LD$_{50}$ (oral, rat) = 100 mg/kg (see footnote 3). AIBN is available from several laboratory supply houses (see footnote 2, 3).

Azobenzene (CAS: 1003-33-3)

Cammenga and co-workers [22, 23] with GEFTA, the German Thermal Analysis Society, suggested azobenzene as a kinetic reference material. It has a reversible, endothermic solid–solid isomerization transition near 120 °C with no mass change during the transition, no side reactions, and goes 100% to completion. It is confirmed first-order with several kinetic publications in the literature (see Table 4). Its endothermic reaction makes it particularly safe for student study but its endothermic nature is not often of interest to those studying kinetics. Azobenzene is commercially available in high purity (see footnote 1, 3, 5).[5] Its LD$_{50}$ (oral, rat) = 1000 mg/kg (see footnote 3).

These four candidate kinetic reference materials show simple first-order reactions. Some reference materials are desired that have reaction order values other than $m = 0$ and $n = 1$.

Cumene Hydroperoxide (CHP) (CAS: 80-15-9)

Cumene hydroperoxide is thought to have a half-order reaction ($n = 0.5$) [24]. It is commercially available and several detailed kinetic studies are available (Table 5). Like DTBP, however, it is a liquid, with a boiling temperature of about 101 °C and is often studied in solution. It is not considered to be particularly toxic with LD$_{50}$ (oral, rat) = 382 mg/kg (see footnote 3). CHP is available from several laboratory supply houses (see footnote 3, 4, 6).

Phenyltetrazolthiol (CAS: 86-93-1)

Chervin and Bodman have provided kinetic data on several autocatalytic nitro decomposition compound reactions including 2-benzyloxy-5-chloro-4-nitroaniline, 3-chloro-4-nitrobenzoic acid, *p*-fluoronitrobenzene, and 5-chloro-2-nitrobenzoic acid. Although these materials are candidate reference materials, they are limited by lack of commercial

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[5] Spectrum Chemicals, New Brunswick, NJ.

Table 5 Kinetic parameters for cumene hydroperoxide

E/kJ mol^{-1}	Log A/s^{-1}	Enthalpy/J g^{-1}	Order	Conditions	Reference
		1874			[64]
100			1.0		[65]
120.6 ± 3.0	14.89 ± 0.56		0.5 ± 0.05		[24]
122.0 ± 3.0	11.25 ± 0.52	1810 ± 50	0.502 ± 0.14	35–85% in cumene	[66]
120 ± 12	–	–	Autocatalytic		[67]
		1034 ± 47		80% in cumene	[68]
		1219 ± 30	2 step	80% in cumene	[69]
176		1875			[58]
		1207			[70]
		1152.75		80%	[71]

Values in *parentheses* are assumed

Table 6 Literature values for phenyltetrazolthiol

E/kJ mol^{-1}	Log (Z)/s^{-1}	H/J g^{-1}	n	m	Conditions	Reference
143 ± 17	20.4 ± 2.4		1.68 ± 0.49	1.32 ± 0.14	ASTM E2070	[26]

Values in *parentheses* are assumed

Table 7 Summary of kinetic parameters

Material	E/kJ mol^{-1}	Log (Z)/s^{-1}	H kJ g^{-1}	n	m
Di-*t*-Butyl peroxide	158.1	15.80	1.34	1.0	0.0
Trityl azide	165.1	19.00	0.724	1.0	0.0
Azobenzene	102.5	11.98	0.254	1.0	0.0
Azobisisobutyronitrile	128.5	15.12	1.24	1.0	0.0
Cumene hydroperoxide	120.6	11.3	1.81	0.5	0.0
Phenyltetrazolthiol	143	20.4	–	1.7	1.3

availability [25]. Phenyltetrazolthiol was selected as a commercially available solid material with a melting temperature of 145 °C (see footnote 2, 3, 4, 5, 6).[6] Its decomposition reaction is confirmed to be autocatalytic. A single interlaboratory test provides reaction order values for m and n as well as activation energy and pre-exponential factor (Table 6) [26]. It is non-toxic with an LD_{50} (oral, mouse) = 1750 mg/kg (see footnote 3).

Summary

An intensive study confirms that no one material is suitable as a kinetic reference material for all the apparatuses, methods, or software. Nonetheless, a "short list" of six candidate materials is offered from which the user may select reference material candidates to meet a particular need. Table 7 provides list of candidate reference materials along with the recommended kinetic values derived from the literature.

Input is requested from the reader for additional kinetic information and literature citations for these materials. In additional, the suggestions for alternative kinetic reference material candidates are welcome.

This study is conducted under the supervision of ASTM International Committee E27 on Hazard Potential of Chemicals and is under the jurisdiction of Subcommittee E27.02 chaired by Mike Oliver of Intertek. It is hoped that this review and these results will lead to a new ASTM International standard tentatively titled Practice for Evaluation of Methods for Kinetic Parameters by Thermal Analysis [27].

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[6] AlfaAesar, Ward Hill, MA.

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