

# Peroxy bleaches

## Part 2. Determination of the thermodynamic and kinetic chemistry of some peroxy compounds

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### Abstract

The thermodynamic and kinetic properties of a series of inorganic and organic peroxy bleaches were determined using adiabatic rate calorimetry and isothermal microcalorimetry. Results are compared to calculated oxygen balance values. The decomposition of the majority of the compounds is complex. Data indicate the need for cooling during the storage and transport for some materials evaluated. Although no overall structure/activity relationship could be established because of the diversity of molecular architectures studied, a combination of decomposition and activation energy data provides a means for hazard and risk classification.

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## 1. Introduction

Part 1 described the use of peroxybleaches in laundry products and the need to establish the thermochemistry of novel ingredients to ensure safe use during storage, transport and processing [1]. Techniques for hazard evaluation were briefly reviewed including calorimetry and theoretical oxygen balance calculations. The present paper describes the application of these techniques for the hazard assessment of peroxybleaches. It includes the calculation of oxygen balance and the determination of thermodynamic and kinetic parameters for a series of peroxy compounds using the adiabatic rate calorimeter (ARC) and the thermal activity monitor (TAM). These novel results are discussed in terms of implications for safety in manufacturing and the supply chain.

## 2. Experimental

Of the experimental calorimetric techniques available the ARC and TAM are most appropriate for determining the thermochemistry of novel compounds using the small samples available at the development phase of projects involving novel compounds. Furthermore, when used in combination, they are a powerful source of data relating to order of reaction, rate of decomposition, onset temperature of decomposition, and time to maximum rate of decomposition (e.g. see Fig. 1). These physico-chemical parameters are crucial to establishing the safety profile of energetic materials such as peroxy compounds.

### 2.1. Equipment

#### 2.1.1. Adiabatic rate calorimetry (ARC)

The ARC was developed to provide time–temperature–pressure data for chemical reactions taking place under adiabatic conditions to aid assessment of thermal hazards. Useful parameters include  $\Delta H$ ,  $E_a$ ,  $T_{nr}$  and self-accelerating decomposition temperature (SADT). The principles on which the method

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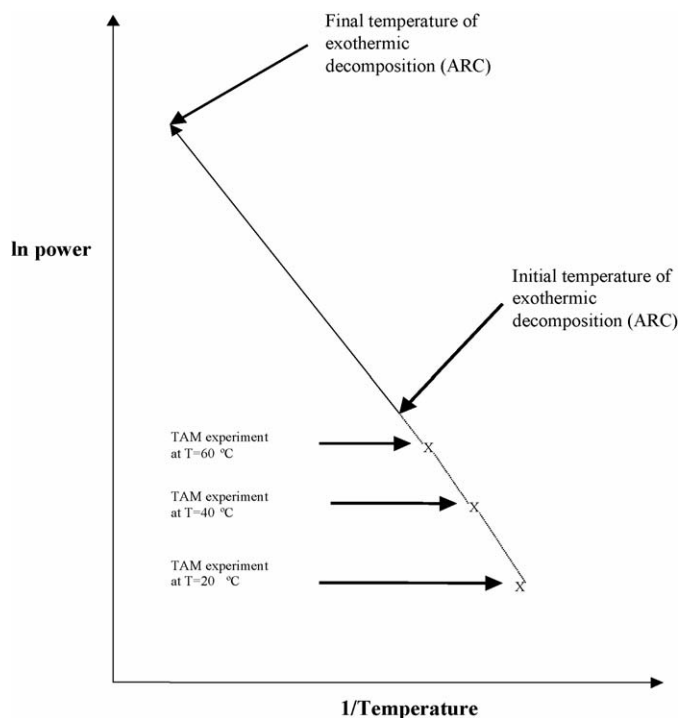


Fig. 1. ARC and TAM data combined.

is based have been expounded elsewhere [2–5]. Also described in the literature are technique variations such as an enhanced adiabatic calorimeter (which allows both the exotherm onset temperature and direct scale-up data for emergency vent sizing to be obtained simultaneously) [6] and a high-resolution adiabatic scanning calorimeter [7]. Applications of ARC for evaluation of thermally unstable compounds such as explosives have also been described [8].

Briefly, ARC data plots of temperature, pressure and self-heat rate versus time provide values for these parameters at the start and end of the exotherm. The heat generated by the exotherm is calculated from

$$\Delta H = \Delta T_{ab} \times C_{p \text{ sample}} \times M_{\text{sample}}/P$$

where  $\Delta H$  is the heat generated (J/mol),  $\Delta T_{ab}$  the true adiabatic temperature rise ( $^{\circ}\text{C}$ ),  $C_{p \text{ sample}}$  the heat capacity of the sample (J/g,  $^{\circ}\text{C}$ ), and  $P$  is the purity of the sample (mol/mol).

The self-heat rate ( $dT/dt$ ) is calculated by

$$dT/dt = A' e^{(-E_a/RT)} ((T_{fs} - T)^n / (\Delta T_{ab,s})) \Delta T_{ab,s} A_0^{n-1}$$

where  $A'$  is the frequency or pre-exponential factor,  $E_a$  the activation energy of the decomposition (J/mol),  $T_{fs}$  the temperature of termination of exotherm in the system,  $\Delta T_{ab,s}$  the adiabatic temperature rise ( $^{\circ}\text{C}$ ) – sample + sample bomb,  $A_0$  the initial concentration of the reactant (at the beginning of the exotherm), and  $A$  is the concentration of the reactant at time  $t$ .

From plots of time to maximum rate ( $t_{nr}$ ) versus reciprocal of absolute temperature the time available before the maximum rate of reaction  $(dT/dt)_{\text{max}}$  can be determined together with the temperature of no return ( $T_{nr}$ ).

Table 1  
Derivation of control and emergency temperature [10a]

SADT	Control temperature	Emergency temperature
20 $^{\circ}\text{C}$ or less	20 $^{\circ}\text{C}$ below SADT	10 $^{\circ}\text{C}$ below SADT
Over 20–35 $^{\circ}\text{C}$	15 $^{\circ}\text{C}$ below SADT	10 $^{\circ}\text{C}$ below SADT
Over 35 $^{\circ}\text{C}$	10 $^{\circ}\text{C}$ below SADT	5 $^{\circ}\text{C}$ below SADT

The SADT is the lowest ambient temperature at which self-accelerating decomposition may occur in a material in the packaging used in transport. It can be calculated from ARC runs thus

$$\text{SADT} = T_{nr} - R(T_{nr} + 273.15)^2 / E_a$$

where  $T_{nr}$  is the temperature of no return  $R$  the universal gas constant (8.314 J/mol K), and  $E_a$  is the activation energy of the exothermic decomposition (J/mol).

SADT values are very important in deciding whether a material should be subject to temperature control during transport or storage, according to the control and emergency temperatures shown in Table 1 [10a]. Chemicals prone to violent decomposition when tested at 50  $^{\circ}\text{C}$  must be subject to temperature control during transport. The ARC used in the present trials was a commercial instrument manufactured by Columbia Scientific Industries of Austin, Texas. Experimental conditions were

- sample bomb type: titanium 1/4 in. diameter STEM (reference 3316);
- sample weight: 1–2 g;
- start temperature: 30  $^{\circ}\text{C}$ ;
- heat step: 5  $^{\circ}\text{C}$ ;
- wait time: 20 min;
- end time: 400  $^{\circ}\text{C}$ ;
- time for complete run: 3–5 days depending on the exothermic activity of test material.

### 2.1.2. Isothermal microcalorimetry using the thermal activity monitor (TAM)

Principles on which the TAM operates are given elsewhere [9] and were mentioned briefly in Part 1 [1].

In the present studies heat flow is plotted against time and the area under the curve corresponds to heat output. Using the following equation  $k$  and  $n$  can be determined:

$$q = k\Delta H (m - q/\Delta H)^n t$$

where  $q$  is the heat output (J),  $k$  the rate constant of the exothermic decomposition reaction,  $\Delta H$  the change in enthalpy (J/mol),  $m$  initial mass of sample (g),  $n$  the order of reaction, and  $t$  is the time (s). Determination of  $k$  and  $n$  is impossible where decomposition is too complex.

Using the equation:

$$\ln k = \ln A' - (E_a/R) \times 1/T$$

the rate of reaction  $k$  plotted against the negative reciprocal absolute temperature enables  $E_a$  to be calculated from the slope and the pre-exponential factor from the intercept with the y-axis.

Half-lives ( $t_{1/2}$ ) can be obtained from the following equations:

- first-order reactions  $t_{1/2} = \ln 2/k$ ;
- zero-order reactions,  $t_{1/2} = m/2k$ ;
- second-order reaction,  $t_{1/2} = 1/mk$ .

The instrument used in these studies was marketed by ThermoMetric Ltd. (Sweden) equipped with Digitam<sup>®</sup> software for instrument control, methods set-up, automation and data evaluation. Heat flow, heat output and time data were converted to ASCII files for import and analysis in Excel 5 and Table Curve 2D packages. Experimental conditions were

- sample vessel: glass insertion ampoule;
- sample weight: 0.5–2 g;
- temperatures: 20, 40, or 60 °C. Not all temperatures were run for every sample because of the time required to equilibrate and calibrate the instrument when the temperature is changed;
- time run: 1–3 days depending on the thermal stability of the test material.

## 2.2. Materials studied

Table 2 lists compounds evaluated together with their purity and supplier code. Sodium percarbonate was sourced from three suppliers. Since the first pair had identical specifications and similar thermal properties results are pooled.

## 3. Results and discussion

### 3.1. Oxygen balance calculations

As discussed in Part 1 [1] the theoretical oxygen balance of a molecule when compared with published scales can be used to indicate the potential explosivity of the compound. The available oxygen content indicates the bleaching potential of

Table 2  
Summary of material evaluated

Code	Compound	Supplier code	Purity
A	Na perborate monohydrate	a	100%
B	Na perborate tetrahydrate	a	100%
C	Percarbonate	b	100%
D	Percarbonate	c	100%
E	Percarbonate	d	100%
F	PAP3	e	95%
G	PAP5	e	95.7%
H	PAP5 wetcake	f	~70%
I	PAP5 granules @amine oxide	e	57% PAP
J	PAP5 gran. @ SAS	e	67.9% PAP
K	PAP5/boric acid	e	30%/70%
L	PAP5/boric acid	e	50%/50%
M	PAP5/boric acid	e	70%/30%
N	PAP7	e	97.0%
O	BIPTA	e	95.0%
P	“Tosylate”	e	N/A

a compound. The theoretical oxygen balance, available oxygen content and explosivity ratings are summarised in Table 3 for comparison with UN classification [10] as discussed in Part 1 [1].

These data would suggest that all three inorganic compounds have high explosivity ratings. However, as explained in Part 1 the oxygen balance should not be considered in isolation but in conjunction with other information. Thus, the categorisation of sodium percarbonate and of both perborates as ‘high hazard’ rating is an artefact of the oxygen balance calculation. Thus, during decomposition of the peroxy salt, part of the oxygen is delivered in the form of water, which is non-oxidising, whereas the calculation assumes that all the oxygen in the molecule is a source of oxidation.

The organic bleaches are classified by suppliers as possessing medium to low explosivity and would formally be classed as of low explosivity hazard rating, taking account of packaging size and chemical composition, i.e. oxygen balance is only a guide.

Table 3  
Calculated oxygen balance values and explosivity ratings

Material	Oxygen balance	Explosivity hazard rating	Available oxygen content (%)
Sodium percarbonate	25	High	15.3
Sodium perborate monohydrate	48	High	16.0
Sodium perborate tetrahydrate	31	High	10.4
PAP3	−157	Medium	6.4
PAP5	−176	Low	5.8
PAP7	−191	Low	5.3
BIPTA	−167	Low	6.1
$\alpha$ -( <i>N,N</i> -dimethyl- <i>N</i> -benzylammonium), 4-peroxy toluic acid tosylate	−194	Low	3.5
Nitrobenzene <sup>a</sup>	−162.6	Low	0.0
Di-nitrobenzene <sup>a</sup>	−95.2	Medium	0.0
Tri-nitrobenzene <sup>a</sup>	−56.2	High	0.0
Glyceryl trinitrate <sup>a</sup>	+3–5	High	0.0
Di-nitrotoluene <sup>a</sup>	−114.2	Medium	0.0
Tri-nitrotoluene <sup>a</sup> (TNT)	−74	High	0.0
Di-nitro- <i>m</i> -xylene <sup>a</sup>	−145.5	Medium	0.0
<i>t</i> -Butyl cumyl peroxide	−256	Low	0.0

<sup>a</sup> Common well-known explosive compounds included for comparison.

Table 4

Kinetic and Thermodynamic data obtained for ditertiary butyl peroxide diluted 1:4 in toluene 'standard'

Thermodynamic data		Kinetic data	
Initial temp (°C)	102	ARC	
Initial self-heat rate (°C/min)	0.006	Decomposition behaviour	$n = 1$
Pressure at initial temp (bar)	1.6	Activation energy (kJ/mol)	158
		(Literature value-ARC) [13]	159
Temp at max self-heat rate (°C)	185	Temperature of no return	104.5
Max self-heat rate (°C/min)	7.58	Self-accelerating Decomposition Temperature °C	101
Pressure at max self-heat rate (bar)	31.8	Time to max rate of exotherm (min) Corrected by $\phi$	845
Final temp (°C) (fully adiabatic)	195.2, 234.6		
Pressure at final temp (°C)	40.6		
Adiabatic temp rise (°C) (fully adiabatic)	93.1, 132.5		
Pressure rise (bar)	36.1		
Heat of decomposition (J/g) (ARC) (literature value) (ARC) [11]	1126, 1314		

Data calculated for a limited homologous series of peracids (Fig. 2) suggests that

- for the same number of carbon atoms, the material with one or more benzyl groups is less stable than the aliphatic compounds: the six carbons in the aromatic ring are not equivalent to hexane.
- stability increases with increased chain length.

### 3.2. Experimental studies

Prior to conducting experiments on trial products using the ARC the operator was calibrated using ditertiary butyl peroxide solution in toluene. Although this material is neither a bleaching agent nor a bleach precursor the exothermic decomposition is known to be simple and the compound has been previously studied using this instrument [11,12]. As illustrated by Table 4 good correlation was obtained for heat of decomposition and activation energy. Thus  $\Delta H_{\text{determined}}$  1126 J/g;  $\Delta H_{\text{reported}}$  1314 J/g and  $E_{\text{a determined}}$  158 kJ/mol versus  $E_{\text{a reported}}$  159 kJ/mol. An  $E_{\text{a}}$  value of 151 has been reported using DSC/DTA techniques [13].

Thermodynamic and kinetic ARC data on test substances are summarised in Tables 5 and 6, respectively; no ARC data are available for compounds K, L and M because of the complexity of decomposition resulting from interference by the boric acid. Kinetic data from TAM experiments are summarised in Table 7.

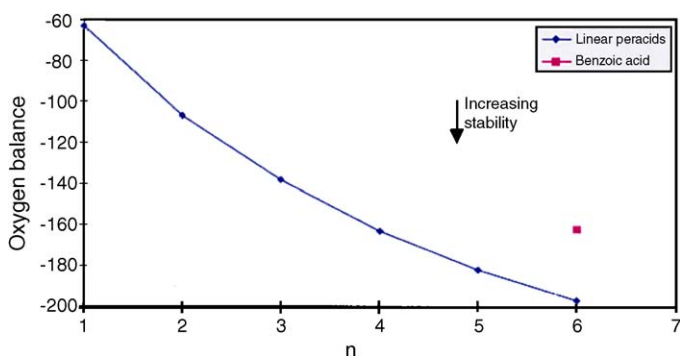


Fig. 2. Oxygen balance for an homologous series  $C_nH_{2n+1}CO_3H$ .

### 3.2.1. Discussion of results for inorganic compounds

Perborates decompose into oxides of boron and oxygen. Data on the decomposition of sodium perborate tetrahydrate in the ARC data gave  $\Delta H$  (25.5 kJ/mol) close to the value obtained using other methods (27 kJ/mol) [14]. The slightly lower ARC value may be attributable to a second exotherm detected. However, since the corresponding  $dT/dt$  is very low these data have been ignored. The decomposition reaction is first-order. The  $t_{\text{nr}}$  of 60.6 °C and SADT of 53 °C suggest 25 kg packages can be stored and transported under normal conditions. The  $t_{\text{nr}}$  is 241 min requiring  $\tau$  of 6000 for calculating requirements for 1 t bags. Such a large extrapolation is hazardous and prevents a meaningful estimate of SADT for tonne quantities of this compound.

Decomposition of the monohydrate is more complex with at least three different mechanisms in operation and with only accurate calculation of  $E_{\text{a}}$  of 145 kJ/mol for the first being possible which compares favourable with 133 kJ/mol obtained by other means [14]. The  $\Delta H$  value of 17.6 kJ/mol obtained from ARC measurements compares with 27 kJ/mol obtained by alternative methods [14]. Because pseudo rate constant versus temperature plots are not straight lines calculation of a reaction order is impossible. Since the SADT exceeds 50 °C the storage and transport of 25 kg packages poses no problems although dry storage conditions maintained below 25 °C are recommended for bulk storage [15].

Based on the Department of Transport classification the supplier material safety data sheets (MSDS) indicate that both perborate mono and tetrahydrates are non-hazardous for international transport [16].

Similarly, sodium percarbonate is classed by the supplier as an oxidiser; storage in a cool dry place is advised. Using material ex-supplier (b) ARC studies suggest a second exotherm occurs during decomposition but this was neglected because of the low  $dT/dt$ . This could explain why  $\Delta H$  (33.8 kJ/mol) is lower than literature values (ca. 60 kJ/mol) using alternative techniques [17]. Differences in  $\Delta H$  for material from different suppliers and that reported in the literature could be attributable to differences in specification of the samples though these data were unavailable. Pressure rate versus self-heat rate plots show decomposition proceeds via at least two mechanisms. The  $E_{\text{a}}$  of 110 kJ/mol



Table 6  
Summary of kinetic properties obtained for a series of peroxy compounds using ARC

ARC	A	B	C	D	E	F	G	H	I	J	N	O	P
Decomposition behaviour	Com	$N=1$	Complex	$N=1$	Complex	com	Compl	$N=1$	Comp	comp	Com	$N=1$	$N=1$
Activation energy, $E_a$ (J/g) <sup>a</sup>	1453	845	701	707	898	465	472	291	315	224	373	262	
Activation energy (kJ/mol) <sup>a</sup>	145	130	110	111	141	116	131	74	104	76	114	69	158
Temperature of no return (°C) ( $T_{nr}$ )	73.0	60.3	65		66.5							37	
Self-accelerating decomposition temperature (°C) (SADT)	66	53	56		60							25	
Time to max rate of exotherm (min) ( $t_{mr}$ )	310	323	1321		681	169	287	103	35	31	688	1590	306
Corrected by $\Phi$	174	241	710		366	83	112	60	20	17	303	662	119

Key to sample code see Table 2.

<sup>a</sup> Average of values obtained self-heat rate plot, activation energy plot, and reaction order plot.

Table 7  
Kinetic data derived from TAM measurements

TAM	D	G	O	P
Rate of reaction ( $k$ ) @ 20 °C			$1.24 \times 10^{-8} \text{ s}^{-1}$	
Half-life				
$t_{1/2}$ @ 40 °C <sup>a</sup>	$6.21 \times 10^{-8} \text{ s}^{-1}$ 129 day	$1.08 \times 10^{-8} \text{ s}^{-1}$ 25 h	640 day	
$t_{1/2}$ @ 50 °C	$6.03 \times 10^{-8} \text{ s}^{-1}$	$1.35 \times 10^{-7} \text{ s}^{-1}$ 4 h	$9.33 \times 10^{-7}$ 59 day	
$t_{1/2}$ @ 60 °C	$1.67 \times 10^{-6} \text{ s}^{-1}$ 5 day	$3.33 \times 10^{-7} \text{ s}^{-1}$ 50 min		9 day
Order ( $n$ )	1	2	1	1
Activation energy				
$E_a$ (J/g)	911	537	239	
(kJ/mol)	143	149	63	

Key to sample code see Table 2.

<sup>a</sup> Average of two samples.

Table 8  
Summary of hazardous properties of sodium percarbonate

Hazard	Precaution
Sensitive to gross contamination	Prevent contamination of raw-material  Select materials of construction e.g. for pipe work, vessels, etc., with care with special attention to quality of surfaces and welds
Sensitive to heat	Avoid over heating stocks and control temperatures where necessary
Sensitive to reducing agents (admixture with organics can be detonatable)	Avoid explosive mixtures  Sequence of addition is crucial Keep away from extraneous combustibles and reducing agents Clean up spillages immediately
Decomposition produces water and oxygen	Efficient mixing essential  Provide pressure relief Prevent oxygen/organic vapour mixtures Process below flash point

Table 9  
NMR data for PAP

$\delta$ (ppm) <sup>a</sup>	Assigned
PAP5	See Fig. 1 PAP5
1.4	(f)
1.75	(e)
2.35 (triplet)	CO <sub>2</sub> H proton from parent acid impurity
2.4	(d)
3.7	(c)
7.7	(b)
7.85	(a)
11.4	CH <sub>2</sub> CO <sub>2</sub> H protons from parent acid impurity
PAP7	See Fig. 1 PAP7
1.35	(f)
1.75	(e)
2.3 triplet	CO <sub>2</sub> H proton from parent acid impurity
2.4	(d)
3.8	(c)
7.7	(b)
7.9	(a)
11.5	CH <sub>2</sub> CO <sub>2</sub> H protons from parent acid impurity

<sup>a</sup>  $\delta$  TMS = 0 ppm.

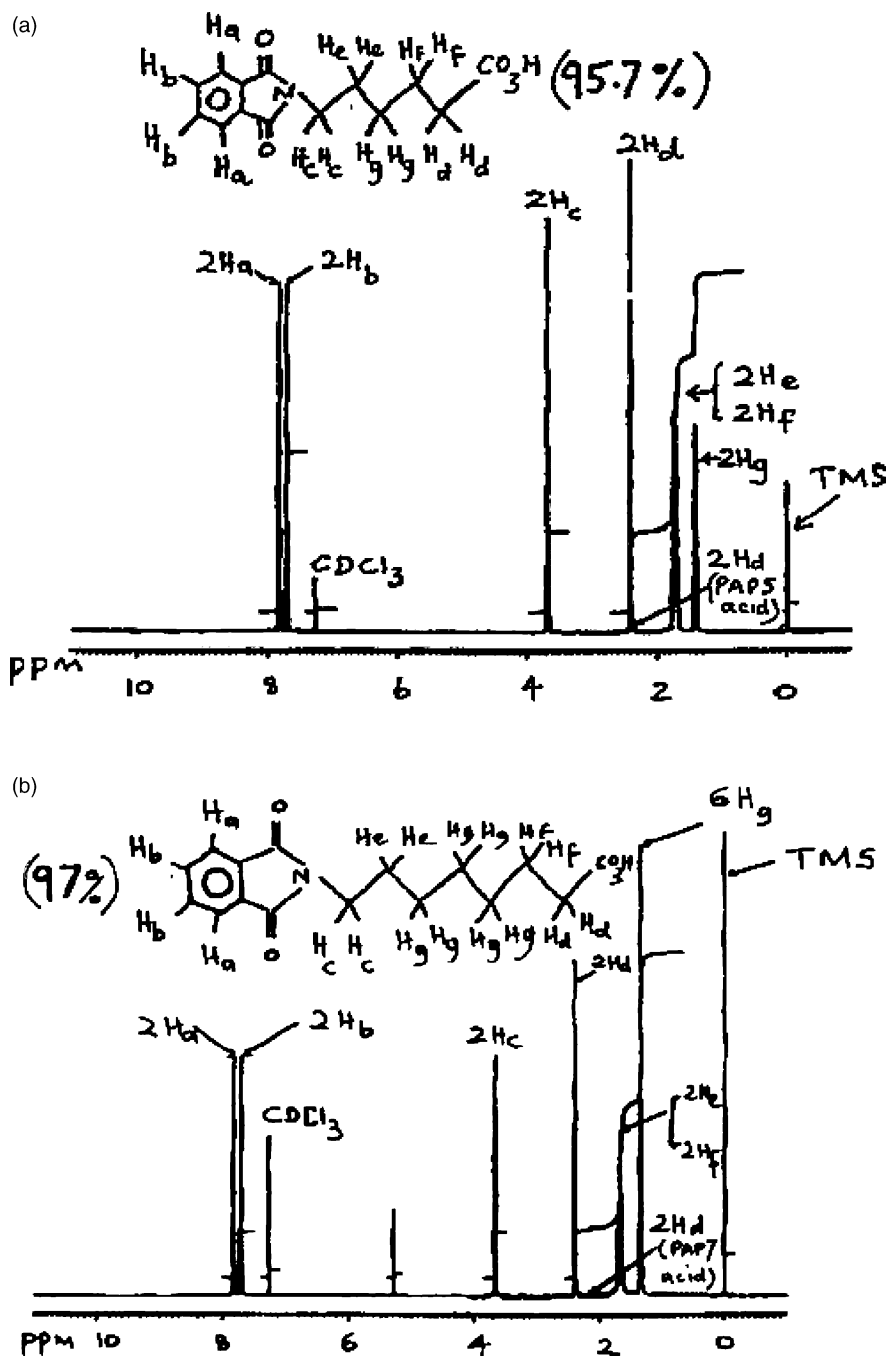


Fig. 3. (a) NMR of PAP5, and (b) NMR PAP7.

for PAP 3, 5 and 7, respectively, and 69 kJ/mol for BIPTA and 158 kJ/mol for  $\alpha$ -(*N,N*-dimethyl-*N*-benzyl ammonium)-4-peroxy toluic acid tosylate. Activation energies from ARC studies are lower than those determined in the TAM because the former represents only the first mechanism of reaction whereas the latter describes the entire decomposition process. As a result of the underestimated ARC  $E_a$  values safety margins have to be built in to their interpretation.

**3.2.2.3. Kinetic parameters.** Plots of rate constant versus temperature were not straight lines and no general order and rate of

reaction could be determined for PAP 3 and 7, i.e. the kinetics of thermal decomposition of the samples could not be described by theoretical equations because of their complex breakdown patterns. BIPTA decomposed via first-order mechanisms and PAP5 followed second-order. This enabled the half-life for PAP5 to be determined and the SADT and temperature-of-no-return to be calculated for BIPTA.

**3.2.2.4. SADT and half-lives.** The SADT of 25 °C for BIPTA requires a control temperature of 10 °C and an emergency temperature of 15 °C. Thus, despite its long half-life, stor-

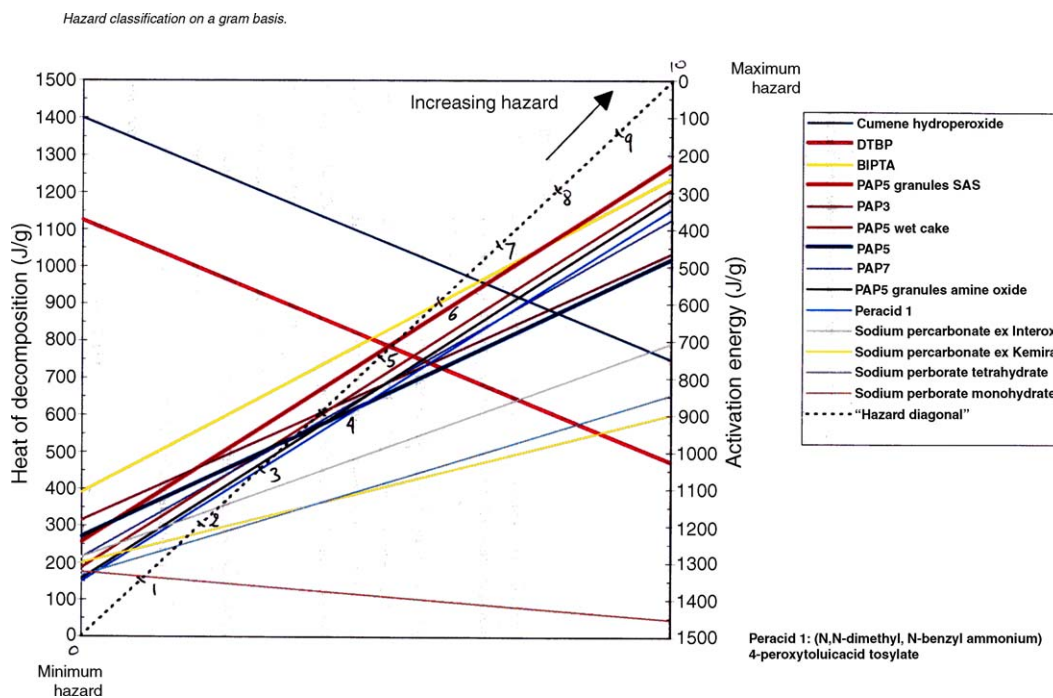


Fig. 4. Hazard classification:  $\Delta H$  vs.  $E_a$  on a mole basis.

age and transportation should be restricted to small quantities under refrigerated conditions. Although no conclusions on storage conditions for the other compounds could be gleaned from ARC measurements, the relatively short half-life for PAP5 and  $\alpha$ -(N,N-dimethyl-N-benzyl ammonium)-4-peroxy toluic acid tosylate under test conditions suggests cooling should be adopted for the storage and transportation of these compounds.

### 3.3. Overall hazard

Both thermodynamic and kinetic properties dictate the hazardous nature of a material: the hazard increases with increasing  $\Delta H$  but decreasing  $E_a$  values. These two parameters may be combined for each compound by plotting  $\Delta H$  on y-axis against  $E_a$  for the first mechanism of decomposition on the second y-axis but in reverse order. A hazard diagonal linking points

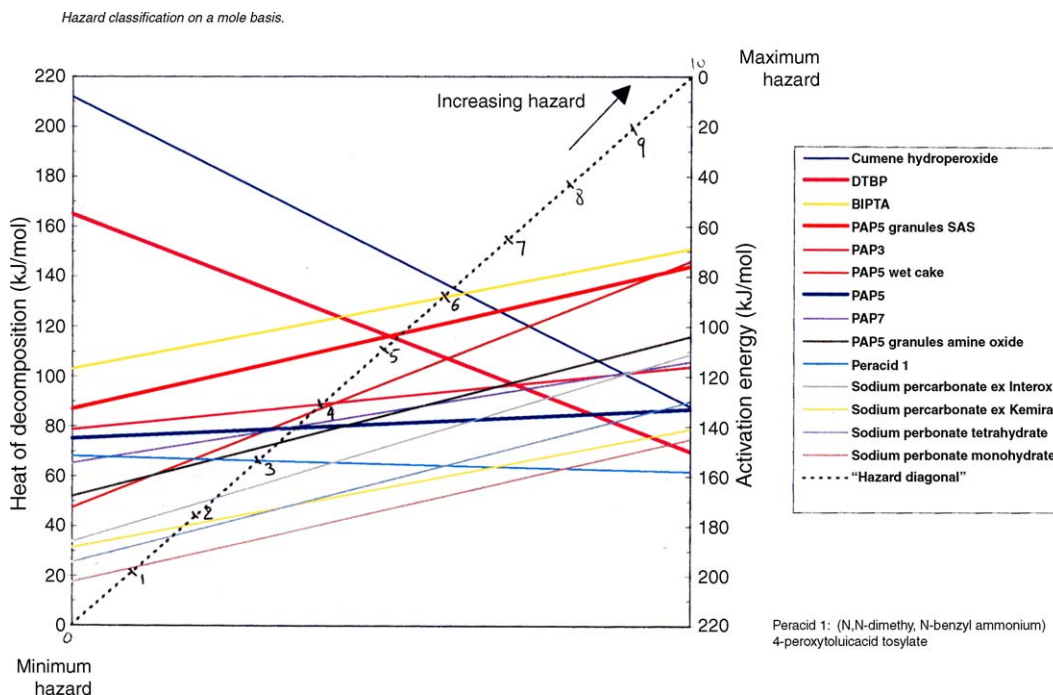


Fig. 5. Hazard classification:  $\Delta H$  vs.  $E_a$  on a gram basis.



