

Calorimetric studies on the thermal decomposition of tri *n*-butyl phosphate-nitric acid systems

K. Chandran · Tarun Kumar Sahoo ·
P. Muralidaran · V. Ganesan · T. G. Srinivasan

Received: 4 August 2011 / Accepted: 21 September 2011 / Published online: 14 October 2011
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Abstract Thermal decomposition of neat TBP, acid-solvates (TBP·1.1HNO₃, TBP·2.4HNO₃) (prepared by equilibrating neat TBP with 8 and 15.6 M nitric acid) with and without the presence of additives such as uranyl nitrate, sodium nitrate and sodium nitrite, mixtures of neat TBP and nitric acid of different acidities, 1.1 M TBP solutions in diluents such as *n*-dodecane (*n*-DD), *n*-octane and isooctane has been studied using an adiabatic calorimeter. Enthalpy change and the activation energy for the decomposition reaction derived from the calorimetric data wherever possible are reported in this article. Neat TBP was found to be stable up to 255 °C, whereas the acid-solvates TBP·1.1HNO₃ and TBP·2.4HNO₃ decomposed at 120 and 111 °C, respectively, with a decomposition enthalpy of -495.8 ± 10.9 and -1115.5 ± 8.2 kJ mol⁻¹ of TBP. Activation energy and pre exponential factor derived from the calorimetric data for the decomposition of these acid-solvates were found to be 108.8 ± 3.7 , 103.5 ± 1.4 kJ mol⁻¹ of TBP and 6.1×10^{10} and 5.6×10^9 s⁻¹, respectively. The thermochemical parameters such as, the onset temperature, enthalpy of decomposition, activation energy and the pre-exponential factor were found to strongly depend on acid-solvate stoichiometry. Heat capacity (C_p), of neat TBP and the acid-solvates (TBP·1.1HNO₃ and TBP·2.4HNO₃) were measured at constant pressure using heat flux type differential scanning calorimeter (DSC) in the temperature range 32–67 °C. The values obtained at 32 °C for neat TBP, acid-solvates TBP·1.1HNO₃ and TBP·2.4HNO₃ are 1.8, 1.76 and 1.63 J g⁻¹ K⁻¹, respectively. C_p of neat TBP, 1.82 J g⁻¹ K⁻¹, was also measured at 27 °C using ‘hot disk’

method and was found to agree well with the values obtained by DSC method.

Keywords Tri *n*-butyl phosphate · Nitric acid · Decomposition · Enthalpy · Activation energy · Heat capacity

Introduction

TBP diluted in aliphatic hydrocarbons, is being used as the solvent for recovering the valuable uranium and plutonium from the spent fuel for over six decades in nuclear fuel reprocessing employing the PUREX process [1]. The choice of TBP has been unchallenged for several reasons such as, easy and economical availability, good physical properties with good selectivity for U (VI) and Pu (IV) with excellent decontamination for most of the fission products, fairly good radiation and thermal stability, and rich availability of data on the extraction behaviour of elements spanning the entire periodic table. Nevertheless, TBP does suffer some disadvantages such as unacceptable aqueous phase solubility, formation of third phase during the extraction of tetravalent metal ions and formation of deleterious degradation products, such as dibutyl phosphate (HDBP), monobutyl phosphate (H₂MBP) which tends to decrease the overall decontamination factors achieved in the reprocessing. The solubility of TBP in aqueous streams as well as inadvertent entrainments to the aqueous streams, during evaporation results in the formation of so called ‘red oil’ leading to violent run away reactions and has caused several accidents in various plants in the past [2–6].

In contrast to the extensive use of TBP worldwide and the importance of the safety issue of the red oil related explosions, the studies on the thermal decomposition

K. Chandran · T. K. Sahoo · P. Muralidaran · V. Ganesan ·
T. G. Srinivasan (✉)
Chemistry Group, Indira Gandhi Centre for Atomic Research,
Kalpakkam, India
e-mail: tgs@igcar.gov.in

behaviour of TBP are very scarce [6–10]. In 1960, Nichols investigated the rate of decomposition of TBP-nitric acid and TBP-nitric acid-uranyl nitrate complexes (organic phase) in closed conditions at Savannah River Laboratories, South Carolina [7]. He calculated the activation energy and pre-exponential factor from the decomposition rate and the values are 112 kJ mol^{-1} and $4.3 \times 10^{10} \text{ s}^{-1}$, respectively. The report indicated that the activation energy remained same for both the cases whilst the pre-exponential factor decreased by an order in the presence of uranyl nitrate. He concluded that the larger molecule of uranyl nitrate presumably gives rise to higher stability. The onset temperature for the decomposition observed by Nichols was $120 \text{ }^\circ\text{C}$. Enthalpy change for the reaction of TBP-nitric acid reported by the author was -251 J mol^{-1} of TBP.

In 1994, Smith and Cavin carried out experiments on TBP-nitric acid solutions of organic and aqueous phases using isothermal calorimeter in an open vent system at Westinghouse Savannah River Site [8]. The values of activation energy and pre-exponential factor reported by them are 97.1 kJ mol^{-1} and $1.35 \times 10^{15} \text{ s}^{-1}$, respectively. The onset temperature for decomposition found by the above authors was $110 \text{ }^\circ\text{C}$.

Paddleford and Fauske performed calorimetric studies on acid-solvate to determine the relationship between vent size and pressure buildup in the event of a run-away reaction as a follow-up to the 1993 explosion at the Tomsk-7 fuel reprocessing plant, Russia [6]. The authors observed an onset temperature for the decomposition of $130 \text{ }^\circ\text{C}$. General conclusions reported by these authors are (i) run-away reaction is possible in open system, (ii) energetics is a strong function of pressure, i.e. does not depend on temperature alone, (iii) energetics increases with increasing nitric acid concentration, (iv) dilution of TBP with dodecane decreases the energetics, no measurable effect is produced by introducing dibutyl phosphate, butyl nitrate and ceric ammonium nitrate.

Barney and Cooper carried out extensive studies on acid-solvate with diluents and metal nitrates [9], using thermogravimetric analyzer coupled with mass spectrometer (TG-MS) and differential thermal analyzer (DTA). The exothermic reaction in the temperature range $140\text{--}175 \text{ }^\circ\text{C}$ was explained by them to be because of oxidation of TBP by nitric acid. They reported -40 kJ mol^{-1} and -58 J mol^{-1} , respectively, as the enthalpy change for the decomposition of acid-solvate (organic phase) and TBP-thorium nitrate and 79.4 kJ mol^{-1} as the activation energy for the decomposition of neat TBP.

Hyder, Savannah River Site, South Carolina, published a report on safe conditions for contacting nitric acid or nitrates with TBP [10]. The author reported an enthalpy change of -479 kJ mol^{-1} for the decomposition of acid-solvate using Nichols data and other thermodynamic data.

Table 1 summarizes the literature reported data on the decomposition of TBP and TBP·HNO₃ (acid-solvate) with enthalpy change, energy of activation and pre exponential term for the decomposition reaction. Keeping the importance of Indian reprocessing scenario, the potential hazardous nature of acid-solvate during evaporation and huge variations in the enthalpy values reported in the literature, the present study is taken up, to generate reliable data on the decomposition behaviour using adiabatic reaction calorimetry. Modern reaction calorimeters offer an elegant way of studying the energy content, enthalpy change and activation energy required in addition to the temperature and pressure excursions resulting from the run-away reactions and also operate with vessels that can withstand the harsh decomposition conditions and corrosive degradation products. Experiments were carried out to study the thermal decomposition of neat TBP, TBP in presence of nitric acid with and without the presence of additives such as uranyl nitrate, sodium nitrate and sodium nitrite, TBP solutions in *n*-DD, *n*-octane and isooctane in either homogeneous single phase or two phase mixtures. Enthalpy change and kinetic parameters for the decomposition reactions have been derived and are compared with the reported data [7–10] as given in Table 1 and discussed.

The heat capacity values of TBP and acid-solvate are necessary to calculate enthalpy change for the decomposition reactions of these compounds. The only heat capacity data found in the literature for neat TBP is $1.445 \text{ J g}^{-1} \text{ K}^{-1}$ at $30 \text{ }^\circ\text{C}$ reported by Nazarko et al. [11]. The authors measured the heat capacity in the temperature range of $10\text{--}150 \text{ }^\circ\text{C}$. Paddleford and Fauske reported a heat capacity value $2.93 \text{ J g}^{-1} \text{ K}^{-1}$ for acid-solvate [6], without giving details of the method or the range of temperature in which the measurements have been carried out. It is presumed that the value would have been computed by Neumann–Kopp addition of heat capacity values of neat TBP and nitric acid at temperature of $25 \text{ }^\circ\text{C}$. In the present work, heat flux type differential scanning calorimeter (DSC) was used to measure the heat capacity of neat TBP and acid-solvate in the temperature range $32\text{--}67 \text{ }^\circ\text{C}$. Heat capacity of neat TBP was also measured using ‘hot disk[®]’ method at $25 \text{ }^\circ\text{C}$ to confirm the values obtained by DSC technique.

Experimental

Chemicals

TBP (Aldrich, USA, 97%), *n*-DD, *n*-octane and isooctane (Lancaster, UK, >99%), Sodium nitrite and sodium nitrate (Loba Chemie, India, 99.5%), Uranyl nitrate hexahydrate (Nuclear Grade, Nuclear Fuel Complex, India), Toluene (BDH Chemicals, UK, >99%) and di-tertiary butyl peroxide (DTBP) (HEL, India) were used as received.

Table 1 A comparison of the thermochemical data of TBP-nitric systems from literature and present study

Sl. no.	Author	System studied	Method/condition	$\Delta H/kJ mol^{-1}$ of TBP	$E_a/kJ mol^{-1}$ of TBP	A/s^{-1}
1	Nichols, 1960 [7]	TBP-HNO ₃	Adiabatic & isothermal experiments/closed	-0.251 ^a	112	4.3×10^{10}
2	Smith and Cavin, 1994 [8]	TBP-HNO ₃ organic	Isothermal calorimeter/open	-	97.1	1.35×10^{15}
3	Paddleford and Fauske, 1994 [6]	TBP-HNO ₃ organic & aqueous TBP-HNO ₃ organic & 30%TBP-70% <i>n</i> -DD	Calorimetry/open	Relationship between vent size and pressure build up	-	-
4	Barney and Cooper, 1994 [9]	TBP-HNO ₃ organic	TGA-MS/DTA/open	-31.9	-	-
		TBP-HNO ₃ organic & aqueous		-39.9	-	-
		Neat TBP		-60.0	79.4	-
		TBP-ThiNO ₃		-58.0	-	-
5	Hyder, 1994 [10]	TBP-HNO ₃ organic	Theoretical calculation	-479.0	-	-
6	Eisenwar et al. [10]	TBP-HNO ₃ organic	Theoretical calculation	-538.7	-	-
7	Present work	TBP·1.1HNO ₃ (organic)	Adiabatic calorimetry/closed vessel/Air ambient	-495.8 ± 10.9	108.8 ± 3.7	6.1×10^{10}
		TBP·1.1HNO ₃ (organic phase) + uranyl nitrate hexahydrate solid		-498.9 ± 4.9	120.1 ± 2.8	3.5×10^{11}
		TBP·1.1HNO ₃ (organic phase) + sodium nitrate solid		-456.3 ± 5.8	128.4 ± 2.5	3.4×10^{12}
		TBP·1.1HNO ₃ (organic phase) + sodium nitrite solid		-426.3 ± 6.3	136.4 ± 3.2	4.1×10^{13}
		TBP·2.4HNO ₃ (organic)		-1115.5 ± 8.2	103.5 ± 1.4	5.6×10^9
		1.1 M TBP/ <i>n</i> -DD equilibrated with 15.6 M HNO ₃ . (Denser acid-solvate and lighter diluent rich organic phases) ^c		^b	86.6 ± 1.4	4.3×10^8
		1.1 M TBP/isooctane equilibrated with 15.6 M HNO ₃ . (organic) ^d		^b	80.6 ± 2.7	1.8×10^7

^a Theoretical calculation^b Enthalpies were not derived because of non-availability of C_p values^c Third phase formation was observed in this system and hence both the denser and lighter phases were taken for studies^d No third phase was observed in this system due to the use of branched diluent

Solution preparation

Acid-solvates with 8 and 15.6 M HNO₃

Equal volumes of neat TBP and 8 M nitric acid were equilibrated in a 15 cm³ glass stoppered centrifuge tube at room temperature for 10 min. The solution was kept idle for 5 min for the separation of phases. The aqueous phase was removed from the solution and same volume of fresh 8 M nitric acid was added to the organic phase and equilibrated again. This process was repeated three times and the separated organic phase was characterized for acidity by titration with 0.1 M sodium hydroxide solution with phenolphthalein as indicator and was found to have the stoichiometry TBP·1.1HNO₃. A similar procedure was followed for the preparation of acid-solvate of neat TBP with 15.6 M HNO₃, whose stoichiometry was characterised to be TBP·2.4HNO₃. Required aliquots of the acid-solvates were taken for calorimetric investigations.

Acid-solvate with solid metal nitrite and nitrates

A measured volume of the TBP·1.1HNO₃ was taken in the calorimetric cell with desired quantity of powdered sodium nitrite, sodium nitrate or uranyl nitrate hexahydrate in solid form and the two-phase mixture was used for the experiments.

1.1 M TBP in diluents

Solutions of 1.1 M TBP was prepared by diluting 29.3 g of neat TBP to 100 mL in a standard volumetric flask with desired diluents such as, *n*-DD, *n*-octane or isooctane. Desired aliquot of the solutions was taken for calorimetric investigations.

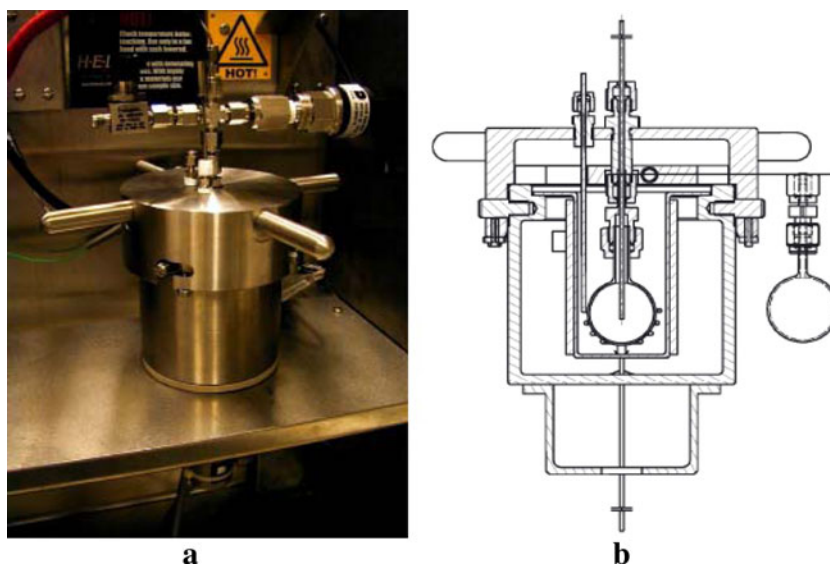
Acid-solvates of 1.1 M TBP/diluent with 8 and 15.6 M HNO₃

Solution of 1.1 M TBP in *n*-DD was equilibrated with 8 M nitric acid as described earlier. Aliquot of the finally separated organic phase containing the acid-solvate was used for calorimetric measurements. Similarly, solutions of 1.1 M TBP in *n*-DD and isooctane were equilibrated with 15.6 M nitric acid and used for calorimetric measurements. The system 1.1 M TBP/*n*-DD formed ‘third phase’ [12] and in this case the heavier acid-solvate phase and the lighter diluent rich phase were together used for the decomposition studies.

Adiabatic calorimeter

An adiabatic calorimeter (model PHI-TEC 1 of M/s HEL, UK) was used in the present studies. The photograph and the schematic diagram of the calorimeter are shown in Fig. 1a and b. The calorimeter consists of stainless steel cylindrical containment vessel lined with cylindrical copper block and a stainless steel lid. The lid of the containment vessel has several leak tight ports to connect test cell, thermocouple, pressure transducer and feed line with ball valve etc. The sample heater wire coiled helically over the spherical test cell heats the sample, whilst three guard heaters at bottom, top and surrounding are used to maintain the adiabatic environment in the calorimeter by maintaining the surrounding temperature equal to that of the sample. These heaters are independently controlled using a PID control algorithm and can track temperature ramps up to 100 °C min⁻¹ and heat the vessel to 500 °C, the limiting temperature of the calorimeter. Stainless steel sheathed K-type thermocouples are provided at bottom, top and side of the vessel for temperature measurement. The

Fig. 1 a photograph of calorimeter, b schematic diagram of calorimeter assembly



calorimeter has a detachable spherical sample cell, made of Hastelloy[®], of capacity 10 cm³ with Swagelok fitting.

A thermocouple (Hastelloy sheathed) placed inside the test cell, in direct contact with the sample measures the sample temperature. The calorimeter has a pressure transducer, to measure the pressure build-up in the range of 0–120 bar with an accuracy of $\pm 0.15\%$, during the course of reaction. Electronics housed in a rack provides all the necessary signal conditioning for the transducers such as those for temperature and pressure and power for heaters. It has facilities such as, (i) PCG2 interface module which communicates the signals between computer and the electronic rack, (ii) A watchdog module which checks for software malfunctions to switch the rack to a safe preset state if the controlling software fails, (ii) thermocouple module, (iv) pressure module, (v) heater control module and (vi) actuator module. WinISO software supplied by M/s HEL, UK, is used for the acquisition of temperature, pressure data as a function of time and controlling the heating pattern. IQ software supplied by M/s HEL, UK, was used to derive enthalpy and kinetic parameters.

Adiabatic calorimetric measurement

Experiments were conducted in a closed vessel with air as ambient. About 2–3 mL of the desired liquid sample with or without the additives as described in Table 3 was taken in the test cell and assembled in the containment vessel with thermocouple placed in direct contact. The cell was heated from room temperature to the decomposition temperature of the sample or to 500 °C (the maximum limit of the calorimeter) in steps of 10 °C in heat-wait-search mode. A calibration procedure (calibrate and calculate steps) was then carried out before searching for exothermic event (search step). In the search step, the guard heaters are set to ‘track’ the sample

temperature such that adiabatic conditions are maintained. The duration of calibration and search period are set for 10 min. At the end of the ‘search’ period, a linear regression is made through the sample temperature data. If the slope of this line has a value (called exotherm) in excess of detection threshold defined when setting up the experiment, then an exotherm is assumed to have occurred and it is tracked adiabatically to completion (track step). The lowest recommended exotherm detection threshold using PHI-TEC 1 is 0.02 °C min⁻¹. If no exotherm is detected, a further calibration procedure is performed before heating the sample stepwise (heat step) using test cell heater. Following a wait period for stabilization (adjust step) the search process is repeated and so on. The size of the step in temperature is user definable and is typically 10 or 15 °C. This process is repeated until an exotherm is detected or a maximum temperature or pressure as specified at the start of the experiment is reached. Temperature and pressure data were logged by a computer and relevant information was displayed on the monitor during an experiment either numerically or graphically. These data were stored on disc at a rate of 5–10 sets per second and used for calculation of enthalpy change and kinetic parameters. Thermal decomposition of di-tertiary-butyl peroxide (DTBP) in toluene (1:4 wt/wt) was performed to test the calorimeter performance, in heat-wait-search mode.

Specific heat determination

Differential scanning calorimeter measurements

A heat flux type DSC, model DSC 821e/700 of M/s Mettler Toledo GmbH, Switzerland, was used for heat capacity measurements. The temperature calibration was carried out by measuring the melting temperatures of indium, tin, lead

Table 2 Heat capacity of neat TBP and TBP-nitric acid complex measured by DSC

Temperature/K	$C_p/J\ g^{-1}\ K^{-1}$					
	TBP		TBP·1.1HNO ₃		TBP·2.4HNO ₃	
	Experimental	Fit	Experimental	Fit	Experimental	Fit
305	1.80	1.805	1.76	1.721	1.63	1.642
310	1.82	1.817	1.76	1.728	1.67	1.658
315	1.83	1.829	1.77	1.737	1.70	1.688
320	1.84	1.841	1.78	1.750	1.73	1.730
325	1.85	1.853	1.80	1.765	1.78	1.784
330	1.86	1.866	1.81	1.783	1.84	1.849
335	1.88	1.878	1.83	1.803	1.92	1.925
340	1.89	1.891	1.85	1.825	2.02	2.010
384						3.103 ^a
393		2.027 ^a		2.169 ^a		

^a Extrapolated value from the fit polynomial

and zinc at heating rates of 2, 5, 10 and 20 °C min⁻¹. The onset temperature of melting at different heating rates were plotted against the heating rates and extrapolated to zero heating rate. The values of the extrapolated onset temperature at zero heating rate were used for temperature calibration. The heat flow calibration was done by using enthalpies of melting of indium, tin, lead and zinc NIST standards, employing a heating rate of 10 °C min⁻¹. The heat flow rate calibration was performed, before every run of the sample, using a disc of sapphire supplied by M/s Mettler Toledo GmbH, Switzerland.

About 10–20 µL of samples were sealed in 40 µL aluminium pans for DSC measurements. A hole was made in the lid of the pan to carry out the heat capacity measurements at constant pressure. DSC measurements on all the samples were carried out in the temperature range 32–67 °C using a heating rate of 10 °C min⁻¹, using ultra high pure (99.999%) argon as purge gas at a flow rate of 50 mL min⁻¹. A disc of sapphire was used as the heat capacity standard. A three segment heating program was employed, with the first isothermal segment lasting for 5 min at initial temperature; the second dynamic segment with a heating rate of 10 °C min⁻¹ and the final isothermal segment lasting for 5 min at the final temperature. The weight of the pan with sample was measured before and after completion of the heat capacity measurements and no measurable change in weight was observed, which indicated negligible evaporation of the liquid sample in the temperature range of measurements.

Hot disk thermal constant analyzer measurements

The specific heat at constant pressure (C_p) was also measured using the 'Hot Disk[®] TPS 2500S Thermal Constants Analyzer', in which the hot disc sensor is placed between two cells holding the liquid whose thermal constants are to be measured. The sample holder is heated in constant current mode for a short period of time. The generated heat dissipates from the sensor into the sample, causing a rise in temperature of the sensor and surrounding sample. The average transient temperature increase of the sensor is simultaneously measured by monitoring the change in electrical resistance. By measuring the temperature vs time response in the sensor thermal transport characteristics of the sample can be calculated.

Derivation of thermochemical parameters

Enthalpy of decomposition reaction

The enthalpy change for an exothermic reaction can be calculated by the following expression

$$\Delta H_r = C_p \times \Delta T_{ad} \times \Phi, \quad (1)$$

where ΔH_r is the enthalpy change of a reaction, C_p the heat capacity of reactant, ΔT_{ad} the adiabatic temperature rise and Φ the phi-factor. The phi-factor is defined by the following expression:

$$\Phi = 1 + \frac{(mC_p)_C}{(mC_p)_S}, \quad (2)$$

where $(mC_p)_C$ and $(mC_p)_S$ are the thermal mass of the sample container and sample, respectively.

Kinetic analysis

Rate constant for an exothermic reaction can be obtained from the calorimetric temperature data by the following expression:

$$k = \frac{\frac{dT}{dt}}{(T_f - T_i) \left(\frac{T_f - T}{T_f - T_i} \right)^n}, \quad (3)$$

where k is the rate constant, n is the order of reaction, dT/dt is the rate of temperature rise. T_i , T_f and T are the temperatures at initial, final and any time t of the exothermic region. The Arrhenius equation given below is used to calculate the activation energy.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

Natural logarithmic form of the above equation can be written as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

a plot of $\ln k$ against reciprocal temperature yields a straight line. Activation energy and pre-exponential factor can be calculated from the slope and intercept, respectively.

Results and discussion

Heat capacity

The heat capacity of neat TBP and acid-solvates (TBP·1.1HNO₃ and TBP·2.4HNO₃) measured by DSC in the present study are given in Table 2 and the values are the mean of five measurements. The standard deviations of the measurements were within ±2%. The measured heat capacity values were fitted to a polynomial by least-squares method and the fit expressions are given in the Eqs. 6–8.

$$C_p^{\text{TBP}} = 8.795 \times 10^{-1} + 2.82 \times 10^{-3}T + 6.071 \times 10^3 T^{-2} \quad (6)$$

$$C_p^{\text{TBP}\cdot 1.1\text{HNO}_3} = -4.5472 + 1.4 \times 10^{-2}T + 1.8926 \times 10^5 T^{-2} \quad (7)$$

$$C_p^{\text{TBP}\cdot 2.4\text{HNO}_3} = -25.32256 + 6.0 \times 10^{-2}T + 8.17896 \times 10^5 T^{-2} \quad (8)$$

The goodness of the fit was determined by computing the standard error using the expression

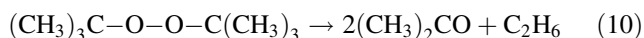
$$\begin{aligned} & (\text{Standard error})^2 \\ &= \frac{(\sum(C_p \text{ measured} - C_p \text{ fit})^2)}{(\text{no. of observations} - \text{no. of coefficients})} \end{aligned} \quad (9)$$

The standard errors of the fit for neat TBP and acid-solvates (TBP·1.1HNO₃ and TBP·2.4HNO₃) were 0.003, 0.04 and 0.01 J g⁻¹ K⁻¹, respectively. The measured heat capacity value of neat TBP at 32 °C is 1.8 J g⁻¹ K⁻¹, which is found to be higher than that of 1.445 J g⁻¹ K⁻¹ reported by Nazarko et al. [11]. Heat capacity of neat TBP measured using ‘hot disk’ method in the present study was found to be 1.82 J g⁻¹ K⁻¹ (mean of seven measurements) which is in good agreement with the values obtained by DSC method and confirms the validity of the present measurements. Thermal conductivity and thermal diffusivity of neat TBP measured using ‘hot disk’ method are 0.117 W m⁻¹ K⁻¹ and 0.067 mm² s⁻¹, respectively. These values are the mean of seven experimental measurements. Evaporation loss of nitric acid limited the heat capacity measurements to 67 °C in the present study.

Paddleford and Fauske reported a heat capacity value 2.93 J g⁻¹ K⁻¹ for acid-solvate, which is the only available data in the literature [6], without mentioning the method and temperature of measurement. Heat capacity value of 1.445 J g⁻¹ K⁻¹ for neat TBP was reported by Nazarko et al. [11] and 1.74 J g⁻¹ K⁻¹ for nitric acid [13] at 30 °C.

Adiabatic calorimeter experiments showed that the acid-solvates TBP·1.1 HNO₃ and TBP·2.4HNO₃ undergo thermal decomposition above 120 and 111 °C, respectively. Calculation of enthalpy change for the decomposition reaction needs the heat capacity of acid-solvates at these temperatures. Heat capacity of acid-solvates at 120 and 111 °C calculated using Eqs. 7 and 8, were found to be 2.17 and 3.1 J g⁻¹ K⁻¹, respectively, and were used for deriving the enthalpy change for the decomposition reaction using Eq. 1.

Di tertiary butyl peroxide (DTBP) undergoes thermal decomposition on heating producing acetone and ethane as per the following equation,



Enthalpy change for the above decomposition reaction in air under closed condition in the present study is found to be -207.5 kJ mol⁻¹, in comparison with the value of -173.6 kJ mol⁻¹, reported by Lizuka and Surianarayanan [14] in nitrogen atmosphere. Nevertheless, the onset temperature for decomposition, the kinetic parameters such as, activation energy and pre-exponential factor of 123.5 °C, 156.7 kJ mol⁻¹ and 6.1 × 10¹⁵ s⁻¹, respectively, agree well with 120.6 °C, 163.76 kJ mol⁻¹ and 7.6 × 10¹⁶ s⁻¹ reported by Lizuka and Surianarayanan. Shaw and Pritchard [15], studied the decomposition of DTBP in carbon-dioxide atmosphere and reported *E_a* and *A* values of 158.2 kJ mol⁻¹ and 6.3 × 10¹⁵ s⁻¹. It is found that the decomposition of DTBP followed the first order kinetics. The results thus confirm the reliability of present calorimetric measurements.

Thermal decomposition of neat TBP

Experimental results obtained in the present study for neat TBP are shown in Fig. 2. The absence of any exothermic event up to 255 °C shows that the TBP is thermally stable up to this temperature. An endothermic peak observed at 255 °C is because of boiling of TBP and beyond which an exothermic event occurs possibly because of the decomposition of TBP vapour. As the temperature rise exceeded the limit (500 °C) of calorimeter, the data obtained in this run could not be used for the derivation of thermochemical parameters. Barney and Cooper reported from TG and DTA investigations that neat TBP is thermally unstable beyond 110 °C. DTA curve for neat TBP showed a steady endothermic peak till its boiling point. TG trace for the neat TBP showed a gradual mass reduction between 170 and 270 °C. Since TG experiments are performed in open,

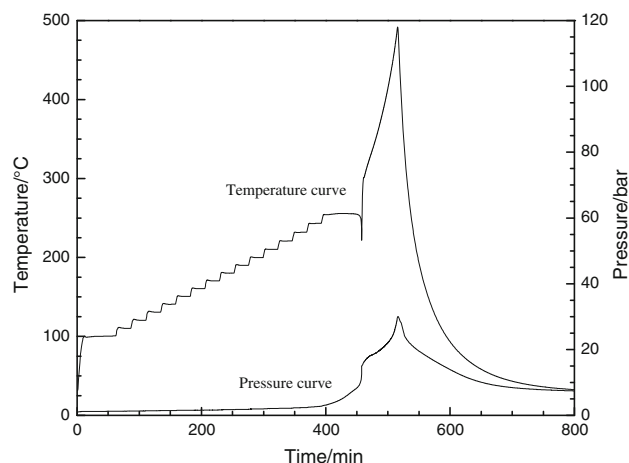


Fig. 2 Variation of temperature and pressure with time for the decomposition neat TBP

Table 3 Systems investigated with onset temperature, pressure and temperature rise in the present study

Sl. no.	System	Phase	Sample ^a		Additive/ mmol	Onset temperature/ °C	$\Delta T/^\circ\text{C}$	$\Delta P/\text{bar}$ Per gram of sample
			Volume/ mL	Weight/g Amount/ mmol				
1	Neat TBP	Organic	2	1.88	–	255	^b	^b
2	TBP-H ₂ O	Organic, Aqueous	0.05	3.6×10^{-4} mol TBP	2.2 g H ₂ O	340	^b	^b
3	Acid-solvate (TBP·1.1HNO ₃)	Organic	2	1.78	–	120	113	26
4	Acid-solvate (TBP·2.4HNO ₃)	Organic	2	1.78	–	111	174	45
5	TBP·1.1HNO ₃ + NaNO ₂	Organic	2	2.06	1.05 mmol NaNO ₂	120	84	23
6	TBP·1.1HNO ₃ + NaNO ₃	Organic	2	2.08	0.83 mmol NaNO ₃	120	79	25
7	TBP·1.1HNO ₃ + UO ₂ (NO ₃) ₂ ·6H ₂ O	Organic	2	2.05	0.3 mmol UO ₂ (NO ₃) ₂	120	94	26
8	TBP + 1 M HNO ₃	Organic, Aqueous	0.01	3.0×10^{-5} mol TBP	2 mmol	270	^b	^b
9	TBP + 2 M HNO ₃	Organic, Aqueous	0.01	3.3×10^{-5} mol TBP	4.2 mmol	150 & 253	^b	^b
10	1.1 M TBP/ <i>n</i> dodecane	Organic	2	1.55	–	235	^b	^b
11	1.1 M TBP/ <i>n</i> Octane	Organic	2	2.08	–	196	^b	^b
12	1.1 M TBP/ <i>n</i> dodecane-8 M HNO ₃	Organic	2	2.38	–	120 & 200	^b	^b
13	1.1 M TBP/ <i>n</i> -dodecane-15.6 M HNO ₃	Denser acid-solvate and lighter diluent rich organic phases	2	1.95	–	49 & 200	47	7
14	1.1 M TBP/isooctane-15.6 M HNO ₃	Organic	2	1.72	–	99 & 85	34	7
15	8 M HNO ₃	Aqueous	2	2.65	–	170	^b	^b

^a Preparation of the samples of TBP·HNO₃/1.1 M TBP/HNO₃, is described in the experimental section

^b Temperature rise exceeded the calorimeter limit (500 °C) and hence experimental runs terminated

evaporation will cause steady mass loss till its boiling point. However, the mass spectrometric investigations by Barney and Cooper show a peak for butene between 110 and 270 °C. Their study also corroborated that the decomposition of neat TBP in the temperature range 110–270 °C is insignificant.

Thermal decomposition of TBP·H₂O

Experimental data obtained for the decomposition of neat TBP and water in the present study showed an exothermic event starting at 270 °C. Again in this run since the exothermic decomposition of TBP resulted in temperature rise beyond 500 °C, the limit of the calorimeter, the experiment was terminated and no thermochemical parameter evaluation could be done.

Thermal decomposition of acid-solvates

Typical experimental data in the present study for the decomposition of acid-solvates, TBP·1.1HNO₃ and

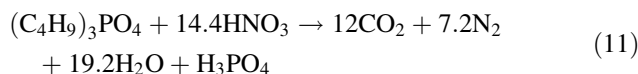
TBP·2.4HNO₃ are shown in Fig. 3. As seen in the figure for the acid-solvate TBP·1.1HNO₃, the sample was initially heated to 100 °C, allowed to stay at this temperature for 40 min to adjust with the surrounding temperature and also for internal calibration. Since no exothermic event was observed, the sample was further heated in steps of 10 °C till an exothermic decomposition occurred. The onset temperature for the decomposition of the acid-solvate was found to be 120 °C which matches with the value of 120 °C reported by Nichols [3], who used an acid-solvate of the composition, TBP·1.2HNO₃ and also by Wagner [7]. Isothermal heat measurements of acid-solvate reported by Smith and Cavin [8] indicated an onset temperature of 110 °C for an open system. The onset temperature of decomposition of acid-solvate reported by Harmon et al. [16] and Barney [9] are 130 and 140 °C, respectively. The higher onset temperatures reported by these authors may be because of the use of open system conditions in their study. Gordon carried out experiments in both closed and open conditions and observed a similar trend in the variation of the onset temperature as cited by Hyder [10]. In closed

system, nitric acid vapour and volatile products of TBP decomposition may react further, resulting in a lower onset temperature. Evaporation of nitric acid from the acid-solvate in open systems may result in higher onset temperatures. The decomposition of acid-solvate was found to be slow in the temperature range 120–150 °C and fast beyond 150 °C as seen in Fig. 3. Barney and Cooper [9] reported similar observation.

The onset temperature for the decomposition of acid-solvate, TBP·2.4HNO₃ as seen in the Fig. 3, is 111 °C which is much lower than the value 120 °C observed for TBP·1.1HNO₃ system. Both these acid-solvates exhibit a sharp increase with spike like feature during the temperature excursion which is attributed to the inability of the instrument to maintain adiabatic conditions because of abnormal heat rise rates of ~300 °C min⁻¹ during the experiment, as the instrument is capable of increasing the surrounding heater temperature only at the rate of 100 °C min⁻¹, resulting in decrease in the temperature sharply after the exothermic event.

The present investigations showed that the decomposition of acid solvates, TBP·1.1HNO₃ and TBP·2.4HNO₃ cause a temperature rise of 113 and 174 °C and a pressure rise of 26 and 45 bar per gram of the acid solvate, respectively, under the conditions of the experiments, in the calorimetric vessel of 10 mL volume with sample volumes of ~2 mL. Both the experiments indicated the formation of non-condensable gaseous products as evident from the pressure curves in Fig. 3 and also resulted in the formation of a viscous residue.

Hyder made theoretical calculations to find out the enthalpy change for the oxidation of TBP by nitric acid and reported a value of -6736.2 kJ mol⁻¹. Complete oxidation of one mole of TBP requires 14.4 mol of nitric acid as given in the Eq. 11.



The nitric acid available in the acid-solvates, TBP·1.1HNO₃ and TBP·2.4HNO₃ used in the present studies, for the oxidation of one mole of TBP amounts to 7.6 and 16.7% of the amount as per Eq. 11. The fraction of enthalpy change corresponding to the available quantity of nitric acid works out to -512 and -1124 kJ mol⁻¹, respectively.

Enthalpy change for the decomposition of acid-solvate, TBP·1.1HNO₃ derived from the experimental data in the present study using Eq. 1 was found to be -495.8 ± 10.9 kJ mol⁻¹ (mean of six replicates). The value closely agrees with that of -479 kJ mol⁻¹ reported by Hyder [10] and -512 kJ mol⁻¹ calculated as per the stoichiometric availability, described in the previous paragraph. Nichols reported a value of -251 J mol⁻¹ of TBP, which is very

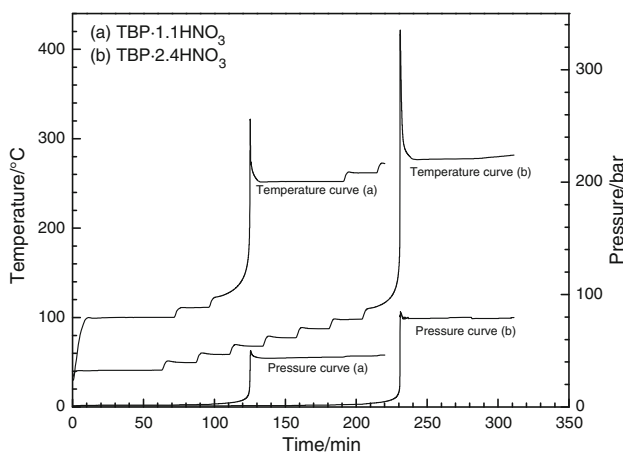


Fig. 3 Variation of temperature and pressure with time for the decomposition of acid-solvates (TBP·1.1HNO₃ and TBP·2.4HNO₃)

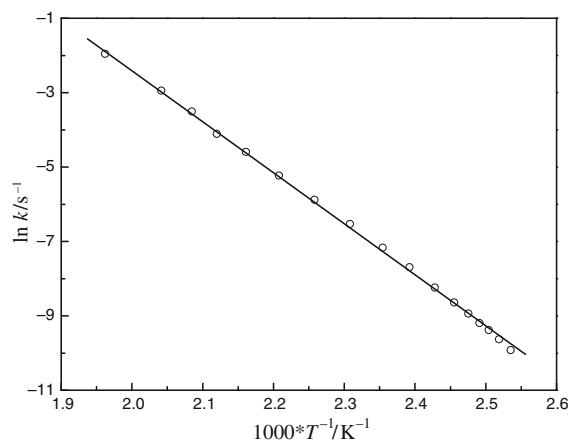


Fig. 4 Arrhenius plot of rate constant versus reciprocal temperature for the acid-solvate TBP·1.1HNO₃

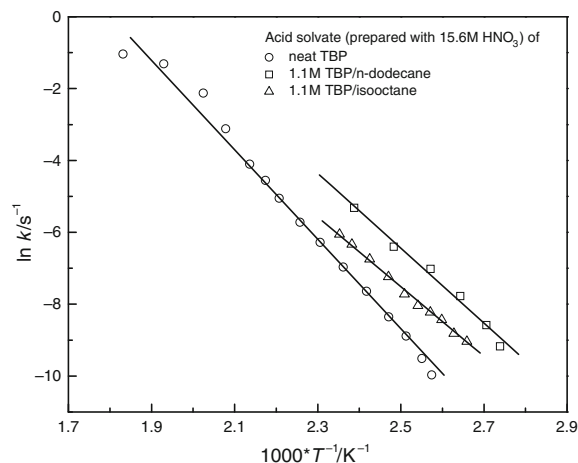


Fig. 5 Arrhenius plot of rate constant versus reciprocal temperature for the acid-solvate TBP·2.4 HNO₃, 1.1 M TBP/n-DD and 1.1 M TBP/isooctane

low, compared to the present measurement. Hyder has attributed the low value of enthalpy change reported by Nichols because of incorrect input of thermodynamic data. Enthalpy change for the decomposition of acid-solvate, TBP·2.4HNO₃, in the present study was found to be $-1115.5 \pm 8.2 \text{ kJ mol}^{-1}$. This value closely agrees with that of $-1124 \text{ kJ mol}^{-1}$ derived as per the fraction of the stoichiometric nitric acid availability.

Rate constant, k , for the decomposition of acid-solvates was calculated from the calorimetric data using Eq. 3. Logarithmic dependence of the rate constant with reciprocal temperature is shown in Figs. 4 and 5. The decomposition of acid-solvates followed first order kinetics, as also reported by Nichols. Activation energy and pre-exponential factor calculated from the slope and intercept, are $108.8 \pm 3.7 \text{ kJ mol}^{-1}$ and $6.1 \times 10^{10} \text{ s}^{-1}$ for the decomposition of TBP·1.1HNO₃ which are in good agreement with the values of 112 kJ mol^{-1} and $4.3 \times 10^{10} \text{ s}^{-1}$, reported by Nichols. For the acid-solvate TBP·2.4HNO₃, the activation energy and pre-exponential factor are $103.5 \pm 3.7 \text{ kJ mol}^{-1}$ and $5.6 \times 10^9 \text{ s}^{-1}$.

Thermal decomposition of acid-solvates in the presence of metal salts

The presence of metal salts such as uranyl nitrate, sodium nitrite and sodium nitrate do not seem to alter the onset temperature for the decomposition of acid-solvate (TBP·1.1HNO₃) from 120 °C in the present study. Rudisill and Crooks [17] studied the decomposition of acid-solvate of neat TBP, in the presence of Al(NO₃)₃, NaNO₃ and KNO₃ using a Reactive System Screening Tool (RSST[®]), and also did not observe any significant change in the onset temperature of decomposition in the presence of the salts. However, the present studies report lower values of the enthalpy of decomposition and higher activation energies. Enthalpy change for the decomposition reaction of acid-solvate in the presence of uranyl nitrate is found to be $-498.9 \pm 4.9 \text{ kJ mol}^{-1}$, whilst the presence of sodium nitrite and sodium nitrate salts resulted in values of -426.3 ± 6.3 and $-456.3 \pm 5.8 \text{ kJ mol}^{-1}$, respectively. Similar trend has been observed by Lambertin et al. [18] in the decomposition of neat TBP in the presence of NaNO₃, NaNO₂ and Precipitated Potassium Nickel Ferrocyanide. Adiabatic temperature rise for the decomposition of acid-solvate and the acid-solvate with uranyl nitrate was found to be nearly the same, whereas it is marginally less in the case of sodium nitrite and nitrate. Sodium nitrite consumes nitric acid from the acid-solvate to form sodium nitrate reducing the availability of nitric acid for the decomposition of TBP, thus decreasing the temperature rise and also increasing the activation energy for the decomposition. The activation energy and the pre-exponential factor obtained

for the decomposition of acid-solvate with uranyl nitrate are $120.1 \pm 0.6 \text{ kJ mol}^{-1}$ and $3.51 \times 10^{11} \text{ s}^{-1}$, respectively. A marginal increase in the activation energy is noticed in the presence of uranyl nitrate over the acid-solvate, thus showing higher stability, which has been attributed because of the larger molecular mass of uranyl nitrate by Nichols. The activation energy and pre-exponential factor for sodium nitrite and sodium nitrate systems are $136.4 \pm 0.3 \text{ kJ mol}^{-1}$, $3.51 \times 10^{13} \text{ s}^{-1}$ and $128.4 \pm 0.7 \text{ kJ mol}^{-1}$, $3.42 \times 10^{12} \text{ s}^{-1}$, respectively.

Thermal decomposition of TBP in the presence of nitric acid

Temperature vs time plot obtained in the present study for a mixture of neat TBP and 1 M nitric acid (two phase,

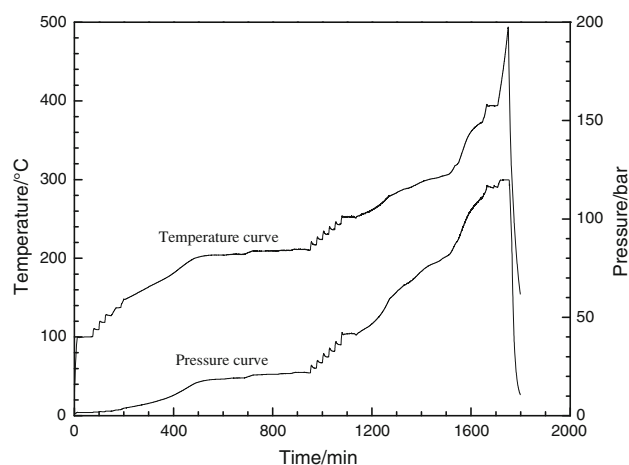


Fig. 6 Variation of temperature and pressure with time for the decomposition of solution of TBP and 2 M nitric acid

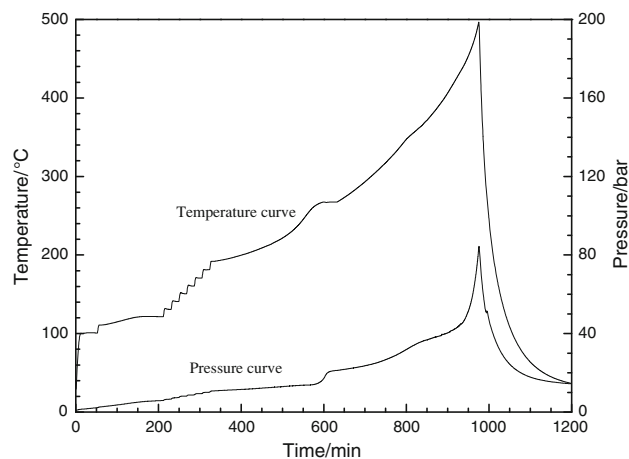


Fig. 7 Variation of temperature and pressure with time for the decomposition of 1.1 M TBP in *n*-DD equilibrated with 8 M nitric acid (organic phase)

organic and aqueous) also showed similar pattern to that of TBP-water mixture. It can be inferred from the results that lower nitric acid amounts are inadequate to initiate the decomposition of TBP. In mixtures of neat TBP and 2 M nitric acid, exothermic reactions were observed at 150 and 257 °C as shown in Fig. 6. The first exothermic reaction at 150 °C possibly is because of the oxidation of TBP by nitric acid and the second event could be because of the thermal decomposition of TBP.

Thermal decomposition of TBP/diluent systems

The decomposition behaviour of 1.1 M TBP/*n*-DD shown in Fig. 7, exhibits exothermic reactions at 235 and 257 °C and an endothermic peak at 265 °C. The exotherm observed at 230 °C could be due to the thermal decomposition of *n*-DD. The endothermic peak at 265 °C and an exothermic event at 257 °C are possibly because of the boiling and thermal decomposition of TBP as seen in the decomposition pattern of neat TBP. Solution of 1.1 M TBP in *n*-octane showed decomposition pattern similar to that of 1.1 M TBP in *n*-DD. Exothermic events observed at 196 and 240 °C, can be assigned to the thermal decomposition of *n*-octane and TBP, respectively. The endothermic peak seen at 250 °C could be because of boiling of TBP.

Figure 8 depicts the decomposition behaviour of acid-solvate derived by equilibrating 1.1 M TBP/*n*-DD with 8 M nitric acid, exhibiting exothermic reactions at 110, 193 and 267 °C. The temperature rise of about 10 and 70 °C were observed in the first and second exothermic events, respectively. The first event could be because of the decomposition of TBP as observed at 120 °C in the cases of acid-solvate experiments and the second event could be because of the decomposition of *n*-DD. The available nitric acid could have been consumed during the decomposition

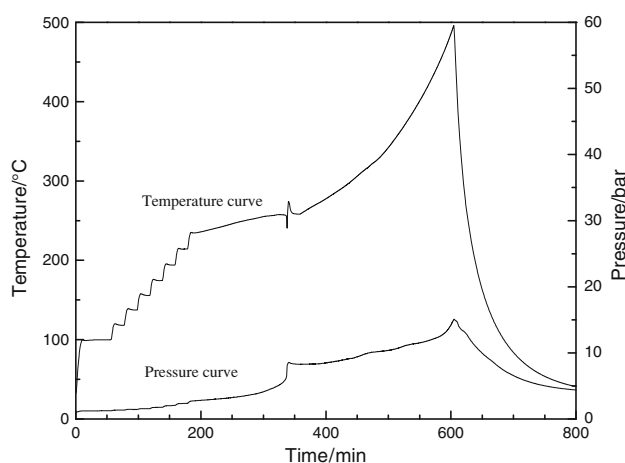


Fig. 8 Variation of temperature and pressure with time for the decomposition of solution of 1.1 M TBP in *n*-DD

of first and second stages itself. The third exotherm observed at 267 °C could be because of thermal decomposition of *n*-DD. In this experiment, also the temperature increase was found to exceed the maximum limit of the instrument, hence the enthalpy change and activation energies could not be derived.

Figure 9 depicts the decomposition behaviour of acid-solvate derived by equilibrating 1.1 M TBP/*n*-DD with 15.6 M nitric acid. The equilibration was found to form third phase with the splitting of the organic into heavier acid-solvate phase and the lighter diluent rich phases. Both the organic phases were quantitatively transferred to the calorimetric vessel to carry out the decomposition studies. This study exhibited an onset temperature of 89 °C with activation energy and pre exponential factor of $86.6 \pm 1.4 \text{ kJ mol}^{-1}$ and $4.3 \times 10^8 \text{ s}^{-1}$, respectively.

Figure 9 also depicts the decomposition behaviour of acid-solvate derived by equilibrating 1.1 M TBP/isooctane with 15.6 M nitric acid. No third phase was observed in this system because of the branched nature of isooctane. The results indicated a lower onset temperature of 99 °C as compared to *n*-DD diluted system, with activation energy and pre exponential factor of $80.6 \pm 2.7 \text{ kJ mol}^{-1}$, $1.8 \times 10^7 \text{ s}^{-1}$, respectively. The reason for the opposing trend in the onset temperature and activation energy between the *n*-DD and isooctane systems is not clear and requires more detailed studies for clear explanation.

Thermal decomposition of HNO_3

The present study on the decomposition of 8 M nitric acid solution showed an endothermic event at 120 °C possibly because of the boiling of nitric acid and an exothermic temperature rise at 170 °C possibly because of the

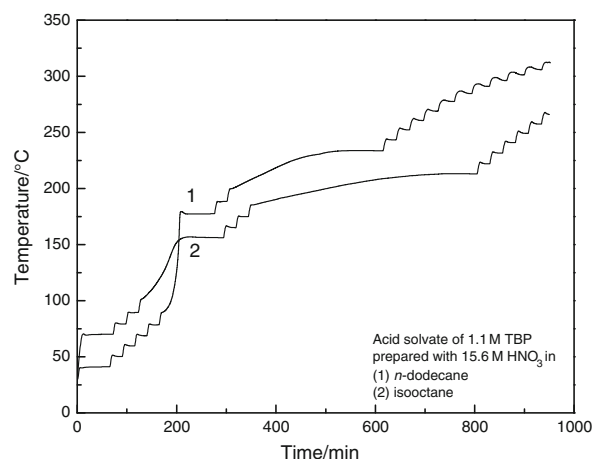


Fig. 9 Variation of temperature and pressure with time for the decomposition of 1.1 M TBP/*n*-DD and 1.1 M TBP/isooctane equilibrated with 15.6 M nitric acid (organic phase)

decomposition of nitric acid. It is reported in the literature that 50–60% nitric acid boils ~ 120 °C.

Conclusions

Thermal decomposition of neat TBP, acid-solvate and solutions of TBP in diluents have been investigated in detail in a closed system in air ambient. Heat capacity at constant pressure of neat TBP and acid-solvate has been measured in the temperature range 32–67 °C by DSC and used for deriving the thermochemical parameters. Neat TBP is thermally stable up to its boiling point. Decomposition of acid-solvate seems to indicate interesting behaviour depending on the stoichiometry. Presence of metal nitrites or nitrates does not have any influence on the onset temperature of decomposition of acid solvate; however their presence increases the activation energy for the decomposition reaction, thus increasing the stability of the system. The enthalpy change, the activation energy and the pre-exponential factor for the decomposition of acid-solvates, are respectively -495.8 ± 10.9 kJ mol⁻¹, 108.8 ± 3.7 kJ mol⁻¹ and 6.1×10^{10} s⁻¹ for TBP·1.1 M HNO₃ and -1115.5 ± 8.2 kJ mol⁻¹, 103.5 ± 1.4 kJ mol⁻¹ and 5.6×10^9 s⁻¹ for TBP·2.4 M HNO₃.

1.1 M TBP in *n*-DD or *n*-octane did not exhibit any accelerated decomposition but 8 M HNO₃ equilibrated solutions of 1.1 M TBP/*n*-DD exhibited lower excursions in temperature and pressure due to the lower concentration of TBP and nitric acid present in those systems. Nevertheless 1.1 M TBP/*n*-DD systems also exhibited a lower onset temperature. The results corroborate unambiguously that a mixture of constant boiling composition of nitric acid (15.6 M) and neat TBP can cause run away reactions once subjected to temperatures of just 89 °C in contrast to the well reported recipe for safe operation <130 °C [5] for avoiding 'red oil' excursions. Possibly the mixture forms 'red oil' in situ and then results in thermal excursion.

Acknowledgements T.G. Srinivasan would like to acknowledge with thanks, The Department of Atomic Energy, India for the award of Raja Ramanna Fellowship. The authors are grateful to Mr. R. Venkatakrishnan, Mr. Abhiram Senapathi and Mr. S. Ganapathy Sankara Subramanian for their help in heat capacity measurements.

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