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Reactive Thermal Hazards of Tributyl Phosphate with Nitric Acid

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ABSTRACT: The accelerating rate calorimetry studies on the tributyl phosphate and nitric acid reactions at various acid concentrations revealed that the conditions for red oil formation may vary with acid strength. The accelerating rate calorimeter studies supplemented with FT-IR characterization of the end products confirmed the formation of red oil at temperatures as low as 75 °C. This study thus strongly advocates for a revisit of safety limits set in the fuel reprocessing plants to prevent red oil formation. The chemical pathway for red oil formation is worked out.

INTRODUCTION

Tributyl phosphate (TBP) has been the workhorse of the PUREX process of the nuclear fuel reprocessing industry for more than five decades. In addition to its application of being a powerful extractant, TBP also finds applications as a plasticizer and as a solvent in inks, synthetic resins, gums, adhesives, and so forth. TBP has a few disadvantages, including the possibility of red oil formation in the presence of nitric acid and nitrates of heavy metals at temperatures exceeding 130 °C.[1,2] Such formation of red oil is an undesirable event which is accompanied by accidental scenarios such as rapid pressurization and explosion. Many red oil related incidents have happened worldwide including Savannah River (1953, 1975),[3,4] Hanford (1953),[5] and Oak Ridge (1959) in the United States, Ontario (1980) in Canada, and Tomsk in Russia (1993).[4] The thermal decomposition of TBP is considered to be the cause of triggering a runaway reaction in the nuclear fuel reprocessing plant. As different cycles of the nuclear fuel reprocessing plant contain nitric acid in different molarities, it is important to understand the reactive thermal behavior of tributyl phosphate at different nitric acid concentrations. Recently, we have reported the thermal behavior pattern of TBP exhibiting vigorous exothermic activity in the 250 °C range using an accelerating rate calorimeter.[6] The present study focuses on the reactive thermal behavior of TBP at varying concentrations of nitric acid. While concentrated nitric acid is used for spent fuel dissolution, 2−3 N nitric acid is being used in extraction cycles and 0.01 N nitric acid is used in stripping cycles of the nuclear fuel reprocessing plant. TBP is known to react with conc. HNO_3 exothermically even in atmospheric conditions.[7]

MATERIALS AND METHODS

Materials. Tributyl phosphate, n-dodecane, and nitric acid used in thermal decomposition studies were of analytical grade obtained from Aldrich Chemicals.

Accelerating Rate Calorimeter (ARC). The working principle, design description, and operational details of ARC are well cited in literature.[8] The schematic diagram of ARC is given in Figure 1. The thermal degradation of TBP in the presence of nitric acid was studied using an ARC supplied by Thermal Hazard Technology (THT), UK. It constitutes a container with its contents maintained at adiabatic conditions with respect to its environment. This is accomplished by constant monitoring of its temperature and suitably adjusting the surrounding temperature to minimize the heat gains or losses from the container. In order to achieve an adiabatic environment over a temperature range of ambient to 450 °C, the ARC is equipped with a sophisticated digital control for the heater system. The calorimeter can be divided into three temperature-control zones, namely, top, middle, and bottom, with each of them equipped with their own control instrumentation. The sample container or "bomb" is attached to a pressure transducer on the top of the chamber for close monitoring of pressure responses. The radiant heater located at the bottom of the adiabatic chamber is meant for heating the sample container at the start of the experiment. ARC operates on the heat−wait−search principle to identify the initiation and progress of exothermic self-heating. It follows the thermal process under the adiabatic mode right from the point of onset. An ARC experiment is initiated under the "heat" mode and to enhance the sample and container temperatures from ambient to 50 °C. It is then kept under "wait" mode for a minimum of 10 min. This is followed by the search mode, wherein the rate of temperature rise of the sample container is monitored. If the self-heat rate is below, say, 0.02 °C/min, the calorimeter re-enters heat mode to further enhance the sample temperature by a prefixed increment (usually 5 °C). This process of "heat−wait−search" is repeated until the system experiences a self-heat rate above the set threshold (Figure 2). It can detect self-heat rate at a sensitivity to the extent of 0.005 °C. When the self-accelerating exothermicity is detected, the sample container is maintained under adiabatic condition as explained earlier. Under these conditions, any increase in sample temperature can be attributed totally to the exothermicity of chemical transformation. When the sample temperature exceeds the preset maximum attainable
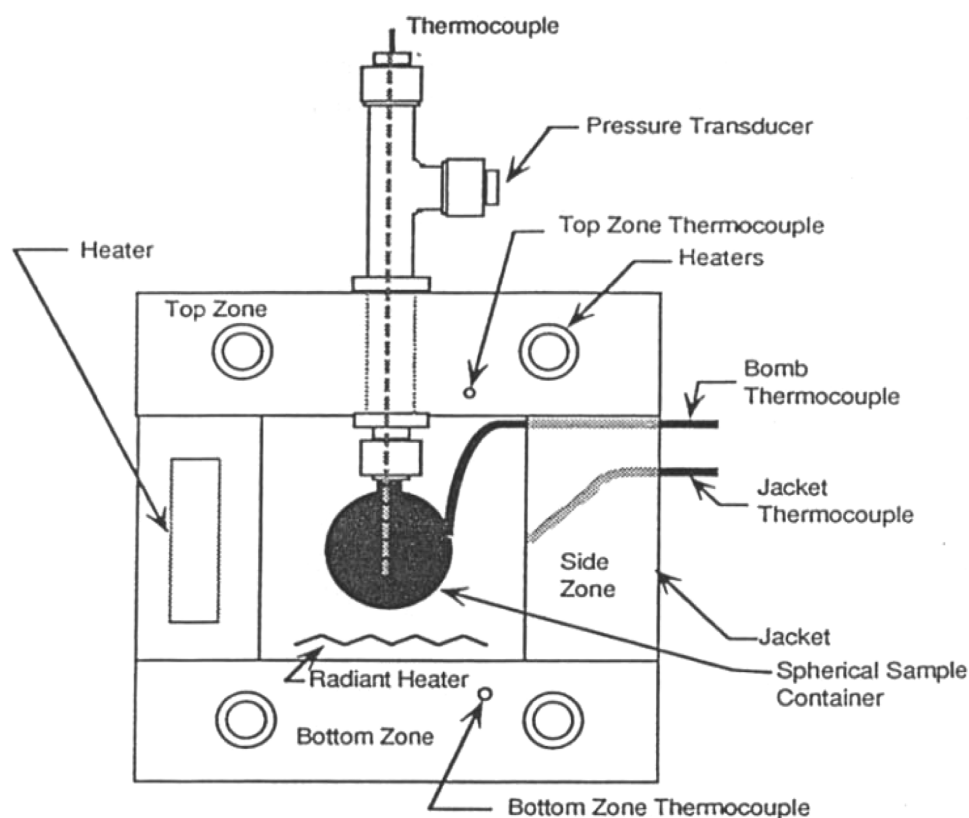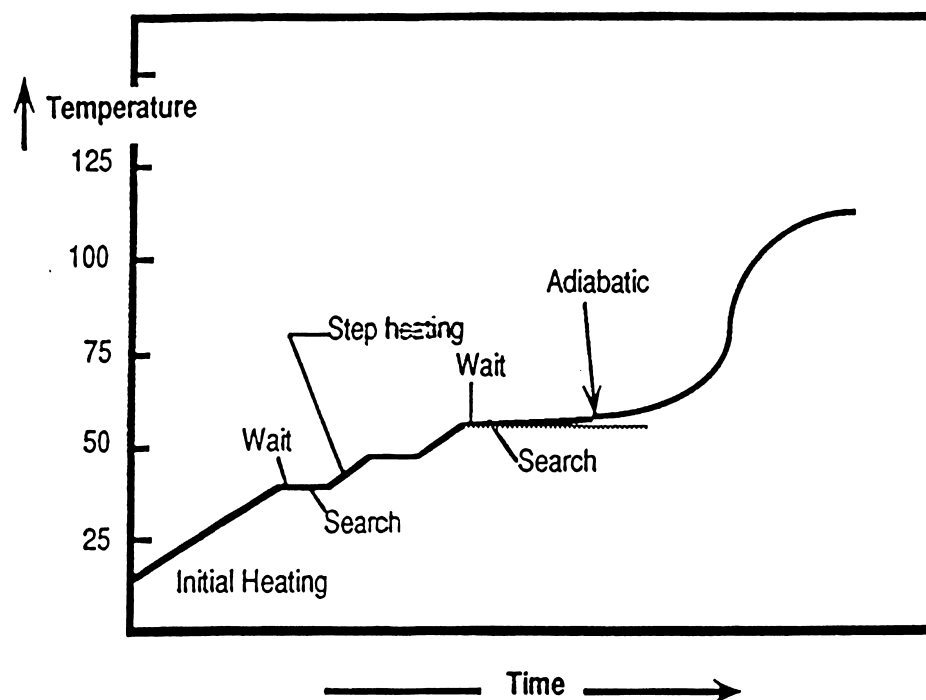
Figure 1. Accelerating rate calorimeter.

Figure 2. Heat–wait–search operation of ARC.

temperature, the ARC run is terminated. The following data plots can be obtained from an ARC experiment.

The self-heat rate vs temperature plot provides information on the onset temperature of the exothermic activity and the rate of energy liberation. The adiabatic temperature rise is given by

$\Delta T_{ad} = [T_F - T_0]$, where T_0 and T_F are the initial and final temperatures of the exotherm.

The temperature vs time plot provides information on the vigor of the exothermic reaction and also the available time period from the onset of exothermic activity to the end of the reaction.

The pressure vs time/temperature plot provides information on the rate of pressure and temperature rise. This is useful for estimating the vent area required for the safe operation of a reactor. From all the above information, the kinetics of the reaction can be studied.

ARC could provide data of temperature, self-heat rate, and pressure in the process of exothermic reactions.[9] Thus, it can accurately determine the onset of the exotherm by maintaining adiabatic conditions.

Procedure for ARC Experiments. About 1 g of 30 wt % of the TBP in n-dodecane and 16 N HNO_3 was taken in varying proportions and loaded into a Hastelloy bomb and its temperature raised incrementally by 5 °C min^{-1} under the heat−wait−search mode, until a measurable rate (0.02 °C min^{-1}) of exothermic activity was detected.

Theory of Adiabatic Thermokinetics. It is a well-established fact that the rate constant of a reaction increases exponentially with temperature. This is demonstrated in the following classical Arrhenius equation

$$k = Ae^{-E_a/RT} \tag{1}$$

where k is the rate constant of the reaction at temperature T, A is the frequency factor, E is the activation energy of the reaction, and R is the gas constant.[8]

The rate of heat loss is a linear function of temperature. The rate of heat loss can be expressed as follows

$$\frac{dc}{dt} = -kC^n \tag{2}$$

where C is the constant of the reactant at time t and n is the order of the reaction.

The first assumption in the interpretation of ARC experimental data is the representation of concentration in terms of temperature differences. The equivalence of temperature and concentration for a simple well-defined chemical reaction is established using the ratio

$$\frac{C}{C_0} = \frac{T_F - T}{T_F - T_0} = \frac{T_F - T}{\Delta T} \tag{3}$$

where C is the concentration of the reacting substance and T the temperature. The subscript 0 indicates some initial condition and F a final state in which the substance has been consumed. Then $\Delta T = T_F - T_0$ is the temperature rise for the reaction. It is equal to the ratio of enthalpy to average specific heat and in the disappearance of the reacting species produces a proportional increase in heat energy. In the accelerating rate calorimeter, part of the heat generated from the reaction is used to heat the sample bomb. The property of the system called thermal inertia determines the amount of heat that is lost to the bomb and is defined as follows:

$$\phi = 1 + \frac{m_b C_{pB}}{m_s C_{pS}} \tag{4}$$

where m_b and m_s are the masses of the bomb and the sample, respectively, and C_{pB} and C_{pS} are the heat capacities of the bomb and the sample, respectively. For the latter, an average value of 0.5 cal °C^{-1} g^{-1} is usually used.

The effect of the thermal inertia is to slow down the reaction by a constant amount. The adiabatic temperature rise of the system is given as

$$\Delta T_{ad} = \phi \Delta T \tag{5}$$

where ΔT_{ad} is the adiabatic temperature rise and ΔT is the temperature rise of the system. In experiments with the ARC the thermal inertia is an important factor in determining the rate of the reaction. For the maximum sensitivity it should be kept low, but a large thermal inertia may be useful in preventing an explosion and for keeping the rate in a measurable range. The total heat generated from the decomposition of the material in the bomb, ΔH, is given by the following equation:

$$\Delta H = m C_p \Delta T_{ad} \tag{6}$$

The question that is basic to the study of relationship of time to explosion is the measurement and extrapolation of data. Extrapolation must involve a concept of concentration since no material can continue to self-heat forever.

When eqs 2 and 3 are used, an additional temperature dependence appears.

$$\frac{dC}{dt} = C_0 \frac{d}{dt} \frac{(T_F - T)}{\Delta T} = \frac{-C_0}{\Delta T} \cdot \frac{dT}{dt} \tag{7}$$

$$m_T = \frac{dT}{dt} = k \left(\frac{T_F - T}{\Delta T} \right)^N \cdot C_0^{N-1} \cdot \Delta T \tag{8}$$

Here, m_T is defined as the rate of temperature increase (or slope of the graph of T vs t), that is, the self-heat rate. To remove this extra temperature dependence, a modified rate is defined as the pseudo rate constant, k^*. It is defined in such a way that its dimensions for any order reaction are reciprocal of time.

$$k^* = k \cdot C_0^{N-1} = \frac{m_T}{\Delta T} \cdot \left(\frac{\Delta T}{T_F - T} \right)^N \tag{9}$$

In practice, k^* is evaluated from experimental data using the right-hand side expression. With the proper choice of N, k^* has the same temperature dependence as k and yields a straight-line graph.

For a first-order reaction, that is, one in which the rate is proportional to the concentration of the reacting substance,

$$k^* = k \tag{10}$$

In many cases the rate of decomposition is approximately proportional to the amount of material undergoing reaction, and n may be taken as 1. Equation 9 then becomes

$$k^* = \frac{m_T}{T_F - T} \tag{11}$$

Values of k^* are thus obtained by the measurement of the rate of decomposition as a function of temperature through the complete course of reaction, and these data are used to obtain the activation energy for the reaction and to interpret the kinetics of the decomposition.[10,11]

■ RESULTS AND DISCUSSION

The time temperature ARC output for reactive thermal behavior of 30 wt % of TBP in dodecane with varying concentrations of HNO_3 (in Figure 3) showed that with increase in acid concentration the onset temperature and the time for onset of exothermic activity preceded. The peak temperature attained was also found to increase with increase in acid normality. In our experiments, with 2 N HNO_3 no exothermic activity was observed. The changes in the pattern of temperature rise indicated the degree of thermal reactivity.
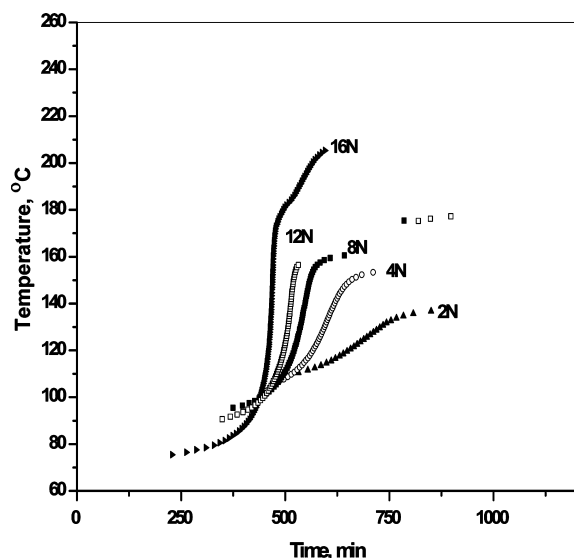
Figure 3. Temperature rise profiles for adiabatic thermal decomposition of 30% TBP with varying nitric acid concentrations in 1:1 ratio. ▲ 4 N, ○ 8 N, ■ 10 N, □ 12 N, ▶ 16 N. (No exotherm observed for 2 N.)

In a recent communication[12] on similar experimental conditions, onset temperature was reported as 89 °C and 14 °C higher than our observations. The discrepancy could be due to the calorimetric sensitivity (obviously higher in this case) and possible errors in establishing the experimental parameters. A total duration of 225 min was required for the heat, wait, and search cycle to reach the onset of exothermic activity, whereas what was reported was observed in a rapid heat cycle at zero time. Considering the high sensitivity of the accelerating rate calorimeter, our data given herein (lower onset, heat–wait–search cycle, and threshold time for onset) could not be favorably compared with previously published data.

The self-heat rate profiles for varying concentrations of acid (Figure 4) showed a clear trend in onset and peak heat release
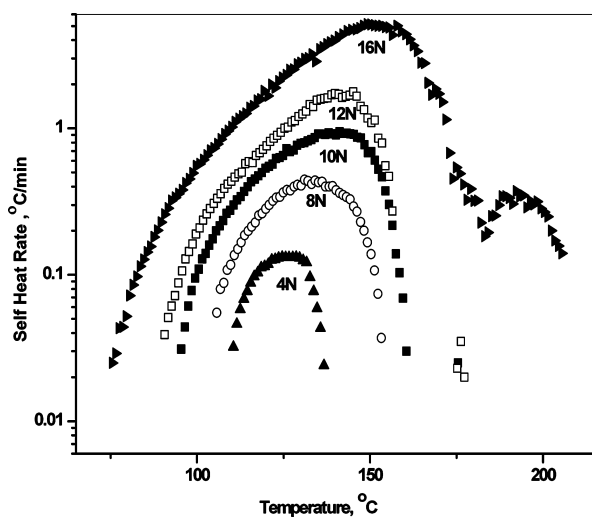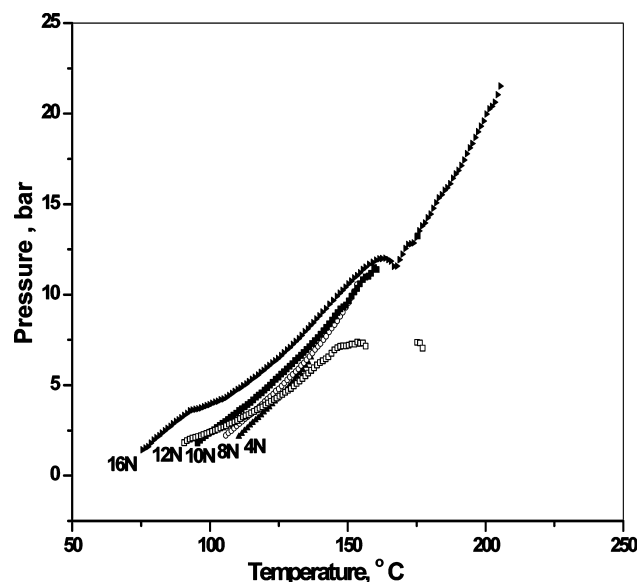

Figure 4. Self-heat rate profiles of adiabatic thermal decomposition of 30 wt % TBP and 70 wt % n-dodecane with varying nitric acid concentrations in 1:1 ratio. ▲, 4 N, ○ 8 N, ■ 10 N, □, 12, N, ▶ 16 N. (No exotherm observed for 2 N.)

rates with increase in acid concentrations. Multiple self-heat rate peaks were seen for 16 N, 12 N, and 10 N concentrations

of acid. The self-heat rate plots again confirmed that the degree of reactivity was dependent on acid concentrations and related to attainment of the peak release rates and temperature. The only reference publication available for comparing our results was by Chandran et al. But the paper did not provide a detailed investigation on varying acid concentrations or information on the self-heat release rates.

A significant pressure release for 1 g of the sample mixture (30 wt % TBP and 70 wt % of n-dodecane with varying concentrations (2−16 N) of HNO$_3$) was observed irrespective of acid concentration (Figure 5). However, with increase in acid

Figure 5. Temperature vs pressure plot of adiabatic thermal decomposition of 30 wt % TBP and 70 wt % n-dodecane with varying nitric acid concentrations in 1:1 ratio. ▲ 4 N, ○ 8 N, ■ 10 N, □ 12 N, ▶ 16 N.

concentration, the peak pressure released also increased. A maximum of 24 bar of pressure was observed for the reaction between TBP and 16 N HNO$_3$. The change in slope of the pressure release curve at 90 and 170 °C observed in the case of 16 N acid treated TBP suggested that the mechanistic pathway leading to product formation was different from the rest of the studies reported.

The thermal reactivity behavior and vigorous self-heating exothermic nature of the system with a significant quantity of pressure release is a concern to the process safety of the fuel reprocessing plant. A detailed discussion on the process safety is given below. The summary of ARC data is presented in Table 1.

The pseudo rate constants ($k*$) were calculated from eq 11. The graph of ln $k*$ versus $1/T$ was plotted for different nitric acid concentrations, and the straight line obtained confirmed the assumption that the thermal decomposition of TBP follows first-order kinetics (data not shown here). From the slope ($-\Delta E/R$) and intercept (ln A) values, the activation energy for the reactions were calculated as 32.69 kCal mol^{-1}, 27.12 kCal mol^{-1}, 23.02 kCal mol^{-1}, 22.17 kCal mol^{-1}, and 32.69 kCal mol^{-1}, and the pre-exponential factors were found as 1.02×10^{16}, 9.74×10^{12}, 5.94×10^{10}, 2.79×10^{10}, and 1.94×10^{9} for 4N, 8N, 10N, 12N, and 16N concentrations, respectively.

$$k = 1.02 \times 10^{16} \exp(-32.69/RT) \qquad (12)$$

Table 1. Summary of ARC Data of a 1:1 Mixture of 30 wt % TBP and 70 wt % *n*-Dodecane with HNO₃ in Varying Concentrations (2N-16N) (No Exotherm Observed for 2N)

S. No.	sample name	thermal inertia Φ	exotherm temperature range °C			corrected adiabatic temperature rise (K)	heat of reaction, ΔH_r (J/g)	Arrhenius parameters	
			onset T	final T	ΔT			E_a, kCal/mol	A, sec⁻¹
1	30% TBP + 16 N HNO₃	6.77	75.47	205.38	129.91	879.49	1398.3	19.79	1.94×10^9
2	30% TBP + 12N HNO₃	6.79	90.65	177.23	86.58	587.88	934.72	22.17	2.79×10^{10}
3	30% TBP + 10 N HNO₃	6.77	95.47	175.37	79.9	540.92	860.07	23.02	5.94×10^{10}
4	30% TBP + 8 N HNO₃	6.83	105.73	153.29	47.56	324.83	516.48	27.12	9.74×10^{12}
5	30% TBP + 4 N HNO₃	6.88	110.51	136.69	26.18	180.12	286.39	32.69	1.02×10^{16}
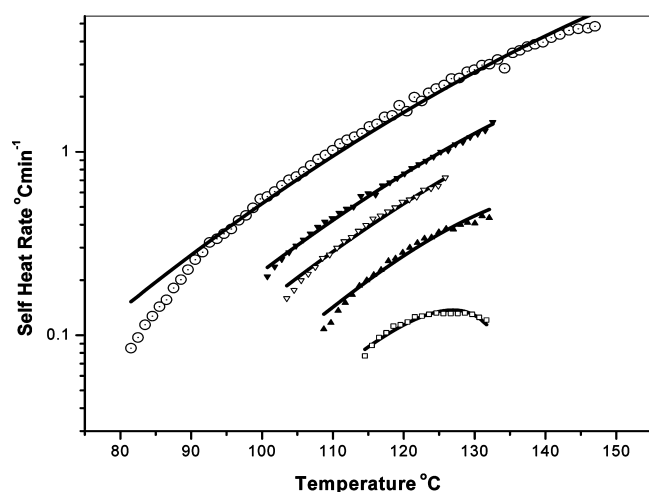
Figure 6. Experimental and predicted self-heat rates for thermal decomposition of 30 wt % TBP and 70 wt % *n*-dodecane with varying nitric acid concentrations in 1:1 ratio. □ 4 N, ▲ 8 N, △ 10 N, ▶ 12 N, ○ 16 N, — Predicted.

$$k = 9.74 \times 10^{12} \exp(-27.12/RT) \tag{13}$$

$$k = 5.94 \times 10^{10} \exp(-23.02/RT) \tag{14}$$

$$k = 2.79 \times 10^{10} \exp(-22.17/RT) \tag{15}$$

$$k = 1.94 \times 10^{9} \exp(-19.79/RT) \tag{16}$$

The heat rates determined with eqs 12−16 were compared with the experimentally obtained heat rates. There is good agreement between the two (Figure 6).

Characterization of End Products Collected from ARC. The FTIR spectrum of the red colored liquid product obtained after the ARC experimentation is stacked is in Figure 7. Tributyl phosphate is an ester which, in the presence of an acid, hydrolyzed into butanol and phosphoric acid. Figure 7 shows that increase in intensity of the peak at 1711 cm⁻¹ (characteristic of C=O stretching vibrations) and decrease at 1013 cm⁻¹ (characteristic of −OH bending vibrations) with increase in acid concentration is suggestive of the oxidation of butanol to carboxylic acid. The gradual decrease in intensity of the peak at 1013 cm⁻¹ is due to the partial oxidation of butanol and was found to be dependent on the acid concentration. The disappearance of the peak at 16 N treated TBP confirms the ability of 16 N acid to oxidize the entire alcohol group to carboxylic acid.
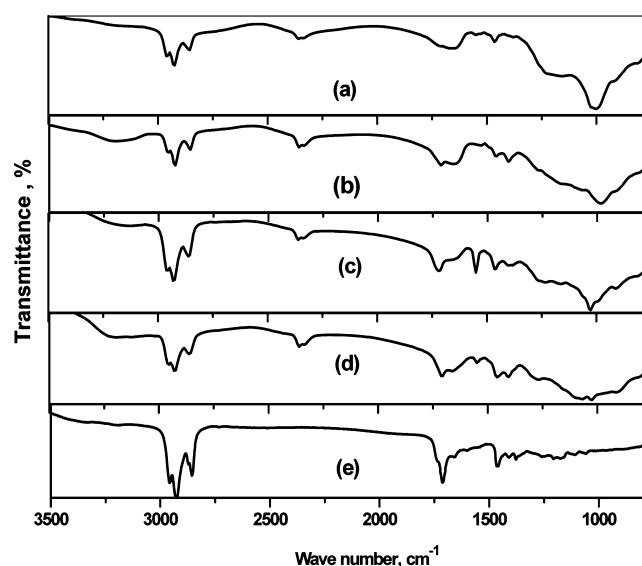

Figure 7. Comparative FTIR of 30 wt % TBP and 70% *n*-dodecane with varying concentrations of HNO₃. (a) 2 N, (b) 4 N, (c) 8 N, (d) 10 N, (e) 16 N.

The conversion of alcohol to carboxylic acid in the presence of nitric acid is reported as a self-heating reaction.[13] The rise in temperature assists in accelerating the oxidative reaction. Also, close observation of Figure 8 shows that all the peaks
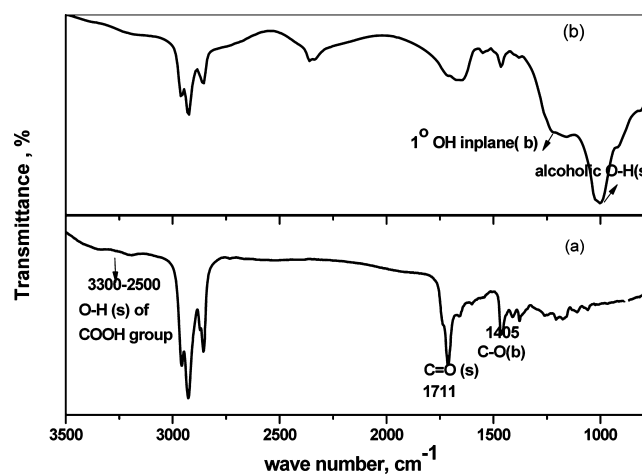
Figure 8. Comparative FTIR of 30% TBP with (a) 2 N and (b) 16 N HNO₃ in the ratio 1:1.

Scheme 1. Predicted Mechanism for the Conversion of TBP to Red Oil
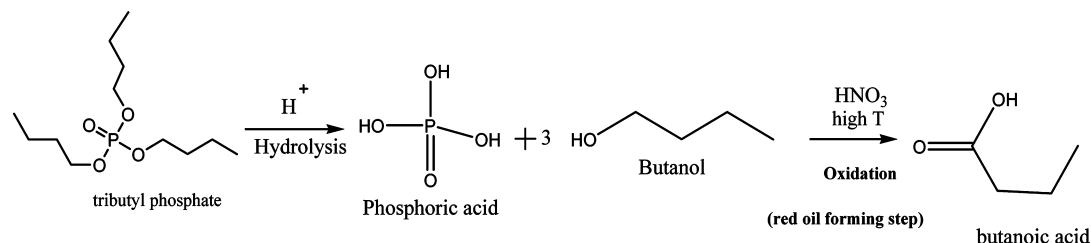
corresponding to −COOH in Figure 8a were absent in Figure 8b. The peaks observed in Figure 8b at 1219 cm^{-1} and 1003 cm^{-1} are due to the 1° −OH in-plane bending and alcoholic −OH stretching vibrations, respectively. This shows that the oxidation of butanol to butanoic acid did not take place in 2 N acid treated TBP. This could be the reason for the absence of exothermic activity even at elevated temperatures. This may be attributed to the inadequate strength of the acid to trigger the oxidation of butanol to butanoic acid. The predicted steps for the conversion of TBP to carboxylic acid are given in Scheme 1.

The physical appearance of the liquids harvested from the ARC sample bomb was deep red in color. The only claim available in the literature on the structure of red oil is of Gordon et al.,[2] and our studies corroborate with them.

Process Safety. The effect of acid strength on TBP diluted with *n*-dodecane is exothermic with possibilities of the reaction vessel getting pressurized. A lowest onset temperature for exothermic activity was recorded at 75 °C with a maximum pressure build up of 24 bar for 1 g of sample. Considering the huge volume of the process vessels and the varying concentrations of acid at different stages in spent fuel reprocessing facility, the possibility of triggering oxidative reactions leading to the formation of red oil cannot be ruled out. Utmost caution is necessary in the monitoring of temperature and pressure excursions and suitable energy dissipation. Pressure relief devices should be considered for safe operation of unit processes in fuel reprocessing. The accelerative effects due to radiolytic products and metal nitrates may further bring about a crisis, which needs attention.

CONCLUSIONS

The accelerating rate calorimetric studies of reactive hazards of TBP-HNO$_3$ supplemented with FTIR characterization of the end products revealed that red oil was obtained at 75 °C in this investigation. The oxidation of butanol formed from the hydrolysis of TBP to carboxylic acid in the presence of nitric acid is the self-heating reaction for red oil formation and energy release. Conditions for red oil formation may vary with acid strength (aqueous layer). The current safety limit in the plant was set at 120 °C to prevent red oil formation, which the present investigation advocates for a revisit. Further studies are required to decide on process safety.

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Notes
The authors declare no competing financial interest.

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