Synthesis and energetic content of red oil

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Abstract

'Red oil' materials, resembling those produced during destructive incidents at Hanford and Savannah River, have been prepared following prolonged heating of uranyl nitrate, nitric acid, tributylphosphate (TBP) and a hydrocarbon diluent either under reflux conditions or within a high-pressure bomb reactor. Phase inversions, a characteristic feature of 'red oil' formation, were observed only when a cyclic hydrocarbon diluent was employed and were not observed when a straight chain hydrocarbon was used. The energetic content of the 'red oil' materials was found to be in the range from 30 to 444 $J g^{-1}$ (7.2–106.1 $cal g^{-1}$) as determined by DSC in open pans in the temperature range 20–350 °C, with a typical value being 200 $J g^{-1}$ (47.8 $cal g^{-1}$). A 'baseline' Purex solution of $UO_2(NO_3)_2(TBP)_2$ released 120 $J g^{-1}$ (28.7 $cal g^{-1}$) upon heating through the same temperature range.

1. Introduction

'Red oil' [1] is a highly dense, energetic, organic-based material which can be formed when uranyl nitrate, nitric acid, tributylphosphate and a hydrocarbon diluent are heated together for prolonged periods. 'Red oil' was found following several well-documented incidents within uranium reprocessing plants in the United States – two at Savannah River (in 1953 [2] and 1975 [3–5]) and one at the Hanford Works in 1953 [6]. Two incidents led to structural damage to buildings housing the vessels. Brief mention has also been made of a similar incident in a Uranium Trioxide Plant in Ontario in 1980 [7], but few technical details are available. All of the incidents occurred when organic materials were inadvertently allowed to enter vessels in which uranyl nitrate solutions were being heated to relatively high temperatures.

In recent years, questions have been raised concerning possible long-term survival of 'red oil' materials within high-level radioactive waste storage facilities, such as the

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Hanford site in Washington. Scenarios have been proposed in which 'red oil' material was inadvertently formed during uranium processing operations and subsequently routed to the waste tanks. If energetic red oil could survive for prolonged periods within a waste tank, this could pose potential safety concerns for waste retrieval and pretreatment operations.

Thus an experimental program was established to prepare samples of material similar to the 'red oil' found during investigation of the Hanford and Savannah River incidents, [2–6, 8–11] to quantify the energetic content of the materials, and to compare the energetics before and after exposure to an alkaline waste simulant material. The results of studies into the synthesis of 'red oil', and subsequent investigation of its energetic content, are documented in this paper. The following paper describes the results of a study of decomposition of 'red oil' by alkaline waste simulant materials.

It should be emphasized that many of the laboratory conditions employed (e.g. temperature, pressure, concentrations) lie well outside the safety control points for the Purex process, and would not be encountered at any point within a normally functioning Purex operation. During previous studies, [12–19], contact of a TBP/hydrocarbon phase with 2–4 M nitric acid at 70 °C for a few hours has been considered representative of 'normal' diluent usage, and thus our use of boiling 6 M nitric acid for periods of 3–8 days should be considered, at the very least, extreme.

2. Synthesis of 'red oil'

2.1. Introduction

The chemical composition of the 'red oil' materials found following the Hanford and Savannah River incidents has not been fully elucidated, and very few data are available with which to compare red oil samples in order to determine their authenticity. Thus we defined a set of criteria to determine whether a sample of a reaction product could be labeled as 'red oil': (1) The sample must be an organic-based material; (2) The sample must be dense, typically in the range 1.10–1.50 g cm^{-3}; (3) The sample must undergo exothermic decomposition, and the initiation temperature for decomposition should be lower than that of the $UO_2(NO_3)_2(TBP)_2$ adduct; (4) Despite the name *'red oil'* , color is *not* taken to be an indicator of energetic content.

Previously, materials described as 'red oil' have been synthesized by prolonged reflux reaction of an aqueous phase comprising uranyl nitrate [$UO_2(NO_3)_2$] and nitric acid, with an organic phase containing tributylphosphate (TBP) and a hydrocarbon diluent. Wagner [21] used such a reflux reaction to obtain an organic phase of density 1.14 g cm^{-3}, and a distillation further concentrated the organic phase to 1.35 g cm^{-3}. This procedure was subsequently repeated using a different petroleum fraction diluent [20] and 'red oil' was again prepared, although the density of the material was not stated. However, Wilbourn has reported that 'red oil' *cannot* be formed when normal paraffinic hydrocarbon is used as diluent [20] and Stieglitz et al.

[22] have prepared dense organic phases employing dodecane diluent which were energetic according to DSC analysis, but were not labeled 'red oil' since DSC traces were virtually identical to those of $UO_2(NO_3)_2(TBP)_2$ adduct.

2.2. Preparative techniques

Three techniques were investigated for the production of 'red oil': (i) Reflux of uranyl nitrate, nitric acid, TBP and a hydrocarbon diluent; (ii) Reflux followed by distillation to produce a high density organic phase; (iii) Use of a high-pressure bomb reactor.

(i) *Reflux*. Prolonged reflux of the aqueous and organic phase components (employing nitric acid concentrations up to 6 M, uranyl nitrate up to 0.161 M, and 30% TBP in hydrocarbon) produced organic phases with densities ranging from 0.97 to 1.25 g cm^{-3} although often at the lower end of this range (see Table 1). During a number of reflux reactions (notably those employing cyclic hydrocarbon components in the diluent) a phase inversion took place, resulting in the organic phase lying beneath the aqueous phase at the end of the reaction. Typical cyclic hydrocarbon components used in these studies are shown in Scheme 1.

| Decalin | Trimethylcyclohexane | Hydrindane | Isopropylcyclohexane | n-Hexylcyclohexane |
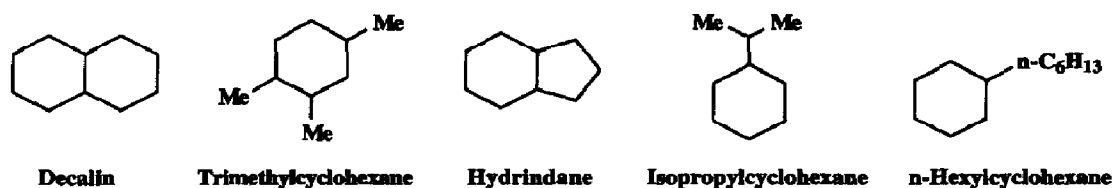
Scheme 1.

The use of pure dodecane as diluent did *not* result in any phase inversion phenomena. Thus 'red oils' of high density are more readily produced when a cyclic hydrocarbon is employed.

(ii) *Reflux/distillation*. In this procedure a reflux reaction was typically carried out for a period of 3 days, and the volume of the reactants then reduced to a third of their original volume by distillation. Using this procedure, 'red oil' materials with densities from 1.09 to 1.45 g cm^{-3} were obtained (see Table 1), and phase inversions were observed when cyclic hydrocarbon diluents were present. This technique offered the advantage of easy scale-up, and was found overall to be the best method for producing 'red oil' of high density.

(iii) *Bomb reaction*. In a typical reaction, 250 ml of aqueous phase and 50 ml of TBP/diluent were sealed into a Parr reactor vessel, and heated with vigorous stirring. The temperature of the vessel was increased to ca. 110–130 °C and held there for several hours, before the vessel was allowed to cool and the organic phase recovered (see Table 2). Although phase inversions were observed on a number of occasions, the densities of the materials were generally $\leqslant$ 1.15 g cm^{-3} and so this technique was not employed to produce bulk quantities of 'red oil'.

Table 1

Summary of 'red oil' samples prepared by reflux procedure

Sample	$UO_2(NO_3)_2$ conc.	HNO_3 conc.	Aqueous volume	Hydrocarbon diluent (vol. ratio)	Organic volume	Reflux time	Concentration by distillation?
1-7-1	0.156 M	4 M	200 ml	Methylcyclohexane/dodecane (9:5)	25 ml	72 h at 760 Torr	No
1-7-3	0.078 M	1 M	200 ml	Methylcyclohexane/dodecane (9:5)	25 ml	24 h at 590 Torr; 72 h at 760 Torr	No
1-9-1	1.161 M	4 M	250 ml	Tert-butylcyclohexane/dodecane (9:5)	50 ml	72 h at 760 Torr	No
1-9-2	0.161 M	4 M	250 ml	Iso-propylcyclohexane/dodecane (9:5)	50 ml	72 h at 760 Torr	No
1-9-3	0.161 M	4 M	500 ml	Decalin/dodecane (9:5)	100 ml	72 h at 760 Torr	No
1-14-1	0.153 M	4 M	250 ml	Decalin/dodecane (9:5)	50 ml	48 h at 760 Torr	No
1-14-3	0.153 M	4 M	500 ml	Trimethylcyclohexane/dodecane (9:5)	50 ml	48 h at 760 Torr	No
1-14-5	0.153 M	4 M	250 ml	Dodecane	50 ml	48 h at 760 Torr	No
1-20-1	0.16 M	4 M	200 ml	Decalin/dodecane(2:1)	30 ml	8 days at 590 Torr	No
1-22-1	0.312 M	6 M	300 ml	Decalin/dodecane (9:5)	50 ml	72 h at 590 Torr	Yes[a]
1-23-2	0.312 M	6 M	200 ml	n-hexyl-cyclohexane/dodecane (7:4)	40 ml	72 h at 590 Torr	Yes[a]
1-23-5	0.312 M	6 M	200 ml	Dodecane	40 ml	5 days at 590 Torr	Yes[a]
1-25-1	0.105 M	6 M	250 ml	Hydrindane/dodecane (1:1)	50 ml	72 h at 590 Torr	No
DEC-39	0.10 M	6 M	1000 ml	Dodecane	250 ml	72 h at 590 Torr	Yes[a]
HYD-40	0.10 M	6 M	1000 ml	Hydrindane/dodecane (1:1)	250 ml	72 h at 590 Torr	Yes[a]
NAPH-41	0.10 M	6 M	1000 ml	Decalin/dodecane (1:1)	250 ml	6 days at 590 Torr	Yes[a]
SPRAY-43	0.10 M	6 M	1000 ml	Hydrindane/Shell Spray Base/dodecane (7:4:3)	250 ml	5 days at 590 Torr	Yes[a]
HYD-48	0.211 M	6 M	1250 ml	Hydrindane/dodecane (7:3)	280 ml	5 days at 590 Torr	Yes[a]

All samples contained 30% TBP by volume in the organic phase.
[a] Distilled to one-third of initial volume.

Table 2
Summary of 'red oil' samples prepared by high-pressure bomb reaction

Sample	$UO_2(NO_3)_2$ conc.	HNO_3 conc.	Aqueous volume	Hydrocarbon used (vol. ratio)	Organic volume	Reaction time/ temperature	Maximum pressure
1-26-1	0.104 M	4 M	250 ml	Trimethyl-cyclohexane/dodecane (1:1)	50 ml	2 h at 115 °C/ 16 h at 100 °C	300 psi
1-27-3	0.104 M	4 M	250 ml	Hydrindane/dodecane (1:1)	50 ml	16 h at 103 °C	660 psi
1-28-1	0.10 M	4 M	250 ml	Shell Spray Base	50 ml	< 15 min at 125 °C	> 2030 psi
1-29-1	0.10 M	4 M	250 ml	Shell Spray Base	50 ml	10 min at 141 °C	> 720 psi
1-31-2	0.104 M	4 M	250 ml	Trimethyl-cyclohexane/dodecane (1:1)	50 ml	15 h at 104 °C/ 30 min at 138 °C	> 500 psi
1-32-1	0.10 M	4 M	250 ml	Decalin/dodecane (1:1)	50 ml	1 h at 70 °C/ <15 min at 125 °C	> 2030 psi

All samples contained 30% TBP by volume in the organic phase.

During these bomb reactions, two rapid overpressurizations were experienced which resulted in bursting of the rupture disc. In the first such reaction, 250 ml of 0.1 M $UO_2(NO_3)_2$ in 4 M nitric acid was being heated with 50 ml of 30% TBP in Shell Spray Base. Approximately 10 minutes after the temperature controller had been increased from 115 °C to 125 °C the rupture disc failed, and a dark red oily material was ejected from the bomb. On the second occasion, the same aqueous phase was being heated with 30% TBP in decalin/dodecane (1:1). At the same temperature controller setting (125 °C), the rupture disc again failed and a similar dark red organic material was produced.

3. Characterization of 'red oil'

Since the literature contained very little characterizing data for 'red oil' [2, 10, 20] a limited effort was undertaken to characterize the principal components of labora-tory-produced 'red oil', and to obtain spectroscopic data for the samples so that their synthesis may be reproduced in other laboratories.

3.1. Nuclear magnetic resonance studies

The ^{1}H NMR spectrum of each 'red oil' material provided a unique fingerprint of the sample, but some generalizations can be made about the gross spectral features (see Fig. 1). The diagnostic resonances of the methylene protons within butyl phosphate groups $[O = P(OC\underline{H}_2CH_2CH_2CH_3)_n]$ lie in a region well separated from other

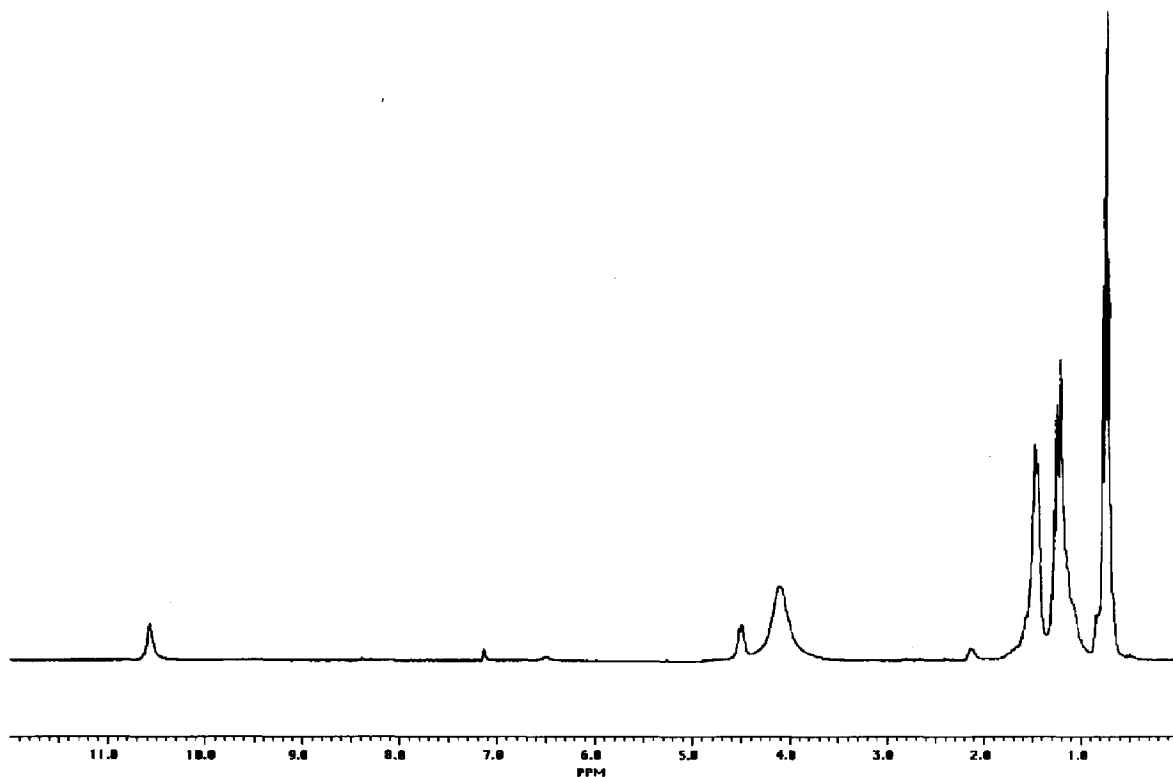Fig. 1. ^{1}H NMR spectrum of 'red oil' sample HYD-40 (see Table 1).

resonances. Generally, two types of α-CH$_2$ groups were seen – one fairly sharp resonance at ca. 4.50 ppm and a more intense, broad resonance at ca. 4.10 ppm. However, these data alone were insufficient to identify the species present. In some cases, broad resonances were observed in the region of 8–10 ppm, which were tentatively assigned to carboxylic acid (–COOH) protons.

The ^{13}C NMR resonances of the α-CH$_2$ groups [O = P(OCH$_2$CH$_2$CH$_2$CH$_3$)$_n$] were observed in the region 67–71 ppm (Fig. 2). In the majority of the ^{13}C spectra, two types of α-CH$_2$ carbons were seen at 68 ppm (fairly sharp) and 69–70 ppm (broad), in agreement with the ^{1}H NMR data. In many of the ^{13}C spectra, resonances were observed which could not be assigned to any of the starting materials – TBP, UO$_2$(NO$_3$)$_2$(TBP)$_2$, or diluent. These resonances were generally observed in the region typical of the carbonyl functionality within a carboxylic acid (ca. 175 ppm) and also in the region from 70–90 ppm which is typical for carbon atoms with attached nitro, nitrate and/or nitrite groups [23]. These resonances could tentatively be assigned to degraded hydrocarbon components resulting from the action of nitric acid upon the diluent.

^{31}P NMR spectra were recorded both at room temperature and at low temperature (−70 °C). At room temperature (Fig. 3), the ^{31}P spectra generally showed a sharp resonance at 5.10 ppm, plus two other broad resonances at ca. 0.5 and 3.5 ppm. At −70 °C, every sample of 'red oil' revealed four ^{31}P resonances at δ −0.5, 2.4, 4.5 and
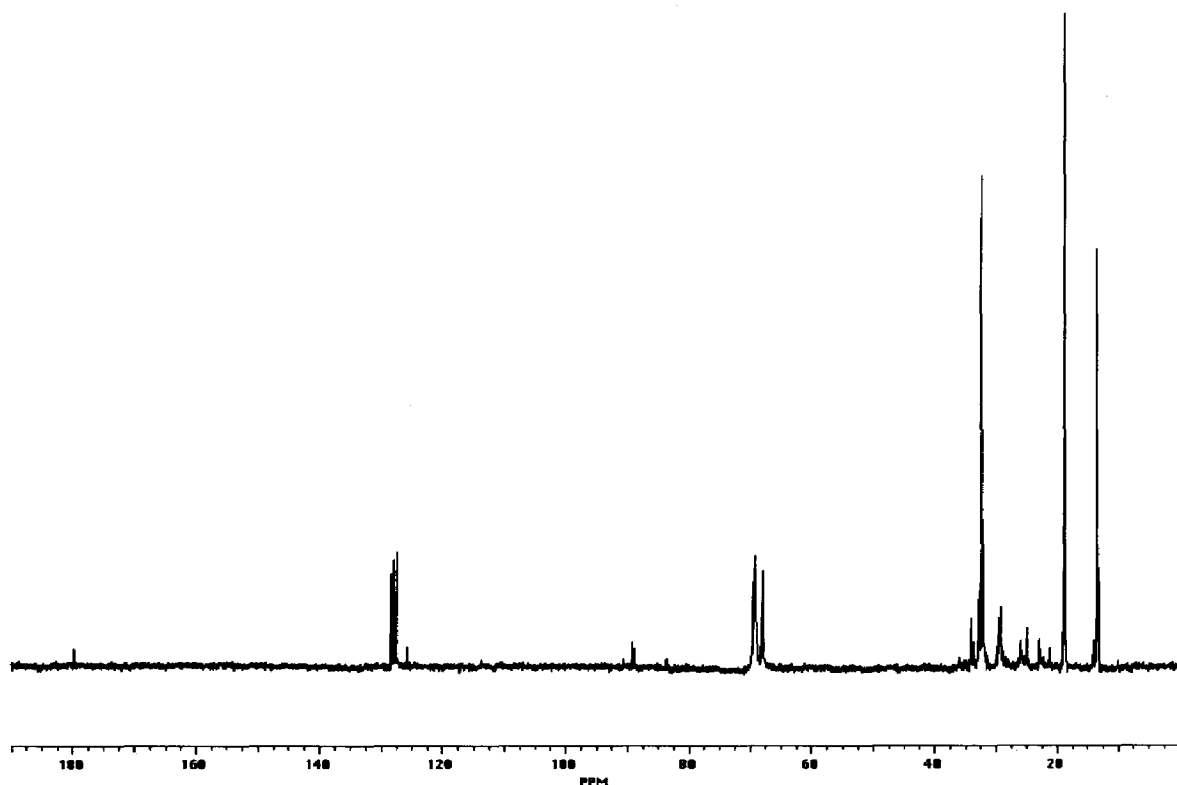
Fig. 2. ^{13}C NMR spectrum of 'red oil' sample NAPH-41 (see Table 1).

5.6 which varied in their relative ratios from sample to sample. Thus the identity of the phosphorus-containing complexes within the 'red oil' samples appears to be independent of the nature of the diluent employed. The resonance at 2.4 ppm was identified as $UO_2(NO_3)_2(TBP)_2$ by comparison of the ^{31}P spectrum of the pure adduct at $-70\,^{\circ}$C.

One important piece of ^{31}P NMR evidence was obtained which suggested that the laboratory-produced 'red oil' samples were a good model for the materials found following the destructive incidents. The dark red organic material from one of the overpressurization events within the bomb reactor was examined by low temperature ^{31}P NMR, and was found to exhibit the same four resonances as all of the samples prepared by reflux or reflux/distillation procedures.

3.2. Infra-red spectroscopic studies

Infra-red spectra of 'red oil' samples were recorded from 4000–400 cm^{-1} as neat liquid films. Some absorptions are common to many of the samples (see Fig. 4): (i) a broad band in the region 1718–1726 cm^{-1}; (ii) a sharp absorption in the range 1660–1664 cm^{-1}; (iii) a band at ca. 1625 cm^{-1}; (iv) one or two strong absorptions in the region 1528–1555 cm^{-1}.

The absorption in the region 1718–1726 cm^{-1}, together with the resonances seen in the ^{13}C NMR spectra at ca. 178 ppm, are strongly suggestive of the presence of
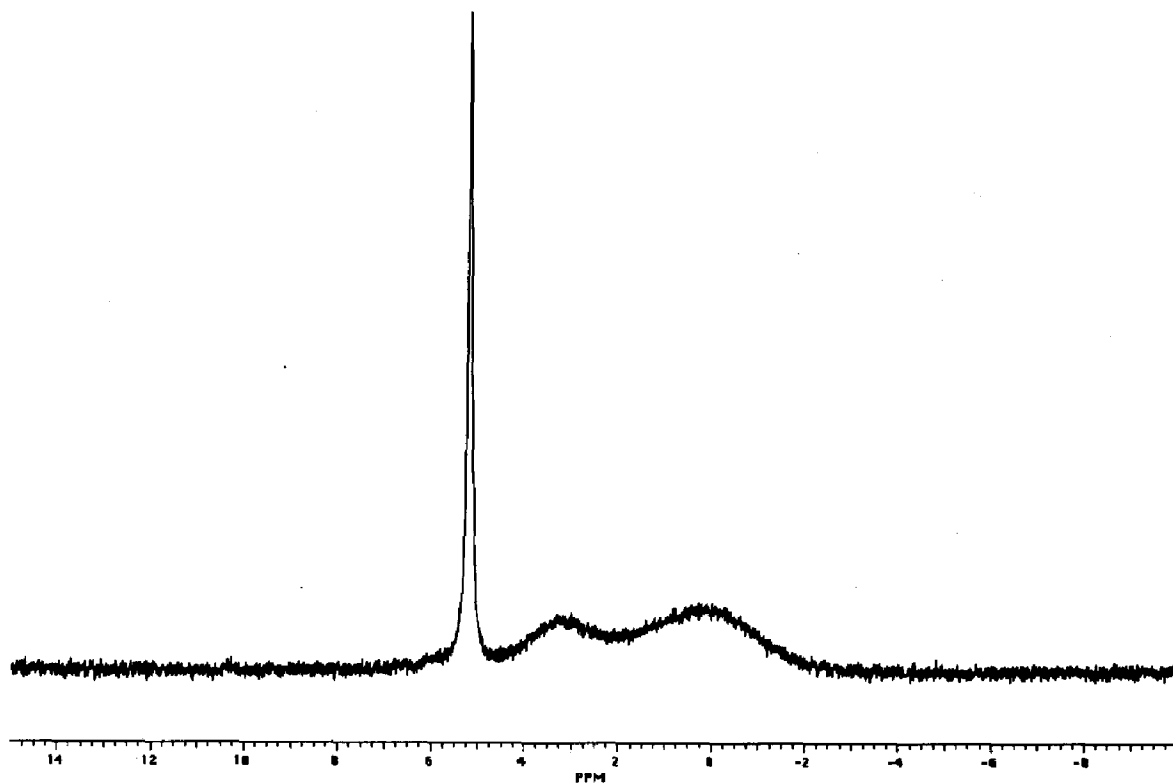
Fig. 3. ^{31}P NMR spectrum of 'red oil' sample NAPH-41 (see Table 1).

carboxylic acids formed by oxidation of hydrocarbons, which almost invariably accompanies the nitration process. The absorptions in the region 1660–1664 cm^{-1} and at 1625 cm^{-1} may be interpreted as the N=O stretching mode in a nitrite (–O–N=O) or nitrate (–O–NO$_2$) group. The band or bands in the region 1528–1555 cm^{-1} are in the range expected for the asymmetric N=O stretch within a primary, secondary or tertiary aliphatic nitro grouping (–NO$_2$).

3.3. Elemental analysis

Elemental (combustion) analysis for carbon, hydrogen and nitrogen was performed on the 'red oil' samples. Typically, the samples comprise between 35% and 55% carbon by weight, with the distilled (highly dense) samples generally lying toward the lower end of this range, while the samples produced by reflux alone had >50% carbon.

Nitrogen content was expected to give a direct indication of the amount of oxidant present in a 'red oil' sample, since the majority of nitrogen present in the samples will be contained within potentially oxidizing groups, i.e. as nitrate or nitrite ion, or as organic nitro, nitroso, nitrate or nitrite compounds. Unfortunately, nitrogen analysis alone cannot determine the relative quantities of nitrogen in ionic and organic forms.
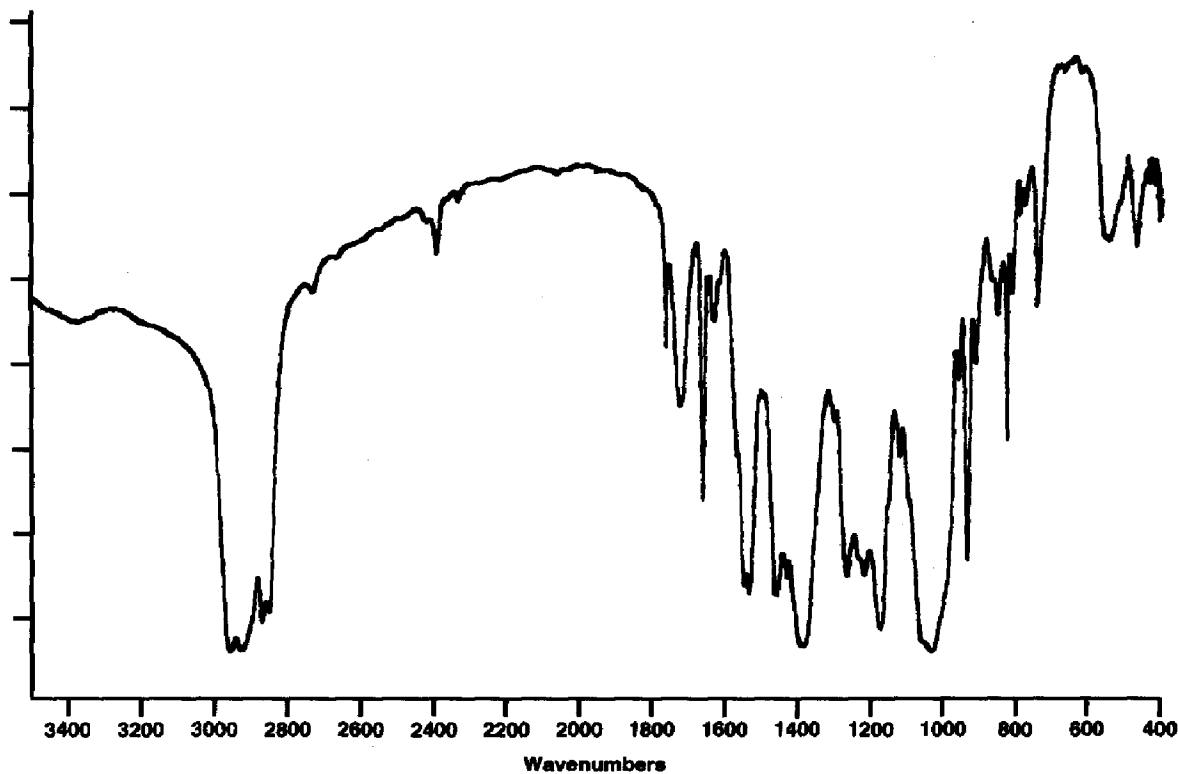
Fig. 4. IR spectrum of 'red oil' sample 1-14-3 (see Table 1).

Nitrogen content of the 'red oil' samples was found to be between 1.5% and 5.0%, with samples prepared in the sealed bomb reactor generally containing a higher percentage than those prepared by reflux in open vessels. This is most likely the result of volatile nitrating species such as HNO_2 and nitrogen oxides, which are able to escape from an open vessel, being kept in contact with the diluent and producing higher degrees of diluent nitration. If nitrogen content is taken as an indication of the quantity of oxidizer present, then 'red oils' appear to be highly fuel-rich, under-oxidized materials. For comparison, $UO_2(NO_3)_2(TBP)_2$ has a nitrogen content of 3.02%, and a fully uranium-loaded Purex stream (30% TBP) would contain ca. 1.6% nitrogen. Since 'red oils' contain approximately the same proportion of oxidant as $UO_2(NO_3)_2(TBP)_2$, exothermic decomposition of isolated 'red oil' samples will suffer from an oxidizer/fuel imbalance and thus release only a small fraction of the energy potentially available within the TBP and/or diluent.

Significant nitrogen content has been found to be a characteristic property of degraded diluent materials. Contact of 20% TBP-odorless kerosene with 4 M HNO_3 at 70 °C for 140 h led to an organic phase containing 1.3% nitrogen [19]. A degradation reaction in which diluent was refluxed with 8 M nitric acid for 6 h, and the nitrogen-containing compounds subsequently concentrated on an alumina column, revealed 2.7% nitrogen content [16]. Furthermore, elemental analysis of one of the organic layers found following the 1975 Savannah River incident [4] showed nitrogen content of 3.06%.

3.4. Gas chromatography/mass spectrometry

In all samples of 'red oil' studied by GC/MS, the major components found were TBP and the hydrocarbon diluent. In many cases, n-butyl nitrate (n-$C_4H_9ONO_2$) was also detected in relatively small quantities (<1%). Despite the fact that n-butyl nitrate can undergo significant exothermic events upon heating [24, 25], no exotherms in the DSC traces could be assigned to decomposition of this compound, presumably due to the relatively low concentrations present. Two potential routes to the formation of n-butyl nitrate may be envisioned: (i) Hydrolysis of TBP under acidic conditions leads to the formation of n-butanol, which can react with nitric acid to produce n-butyl nitrate [26]; (ii) Direct reaction of TBP with a range of metal nitrates, including uranyl, produces n-butyl nitrate in good yields [27].

Apart from butyl nitrate, GC/MS analysis did not conclusively identify any nitrated hydrocarbon species in the 'red oil' samples. However, this should not be taken to imply that these species are not present, and indeed the NMR, IR and elemental analysis studies strongly indicate that these materials are present. Mass spectroscopy of nitroalkanes using electron impact techniques can result in cleavage of the R–NO_2 bond, and subsequent observation of only the $R^{.+}$ hydrocarbon fragment. GC/MS analysis did indicate the presence of butanoic and hexanoic acids in one sample, while alcohols containing eight- and nine-carbon chains were found in two other samples.

4. Energetics of 'red oil' samples

4.1. Introduction

Previously, little attention has been focused upon the energetic properties of 'red oil' as an *isolated* material [21]. 'Red oil' materials have been investigated by heating with further quantities of nitric acid and/or uranyl nitrate until an energetic reaction was observed, but the energy release was *not* an accurate measure of that contained within 'red oil' itself, but rather that of 'red oil' in the presence of additional oxidant.

Differential scanning calorimetry (DSC) was used to provide a quantitative measure of the energetic content of the 'red oil' materials. The DSC behavior of the adduct $UO_2(NO_3)_2(TBP)_2$ has been reported to consist of an exotherm at 225 °C (magnitude 390 J g^{-1}) and an endotherm at 289 °C (255 J g^{-1}) [22]. The exothermic event is proposed to be due to the oxidation reaction between two nitrate groups and two n-butyl groups, while the endothermic reaction is suggested to be due to thermal degradation of the remaining butylphosphate groups to produce butene.

4.2. Experimental results

To confirm the reported DSC behavior of $UO_2(NO_3)_2(TBP)_2$, an aqueous phase containing 4 M nitric acid and 0.14 M uranyl nitrate was contacted with an organic

phase containing 30% TBP in dodecane/decalin (1:1). DSC analysis of the organic phase revealed an exotherm at 232 °C (118 J g^{-1}) and an endotherm at 304 °C (68 J g^{-1}). The energy released was less than that reported for $UO_2(NO_3)_2(TBP)_2$ [22], since the present experiment used a solution of $UO_2(NO_3)_2(TBP)_2$ in diluent rather than the pure adduct.

An aqueous phase containing 4 M HNO$_3$ and 0.153 M $UO_2(NO_3)_2$ was then refluxed with 30% TBP in dodecane for 48 h to produce a floating yellow organic phase (sample 1-14-5 in Tables 1 and 3). DSC of the organic phase revealed energetic behavior very similar to the phase obtained above without any heating [exotherm at 230 °C (115 J g^{-1}) and endotherm at 302 °C (52 J g^{-1})]. Thus after 48 h of reflux, $UO_2(NO_3)_2(TBP)_2$ is still the dominant source of energy within the organic phase, and no additional exotherms from any new energetic species could be observed.

In a further experiment, 6 M HNO$_3$ and 0.312 M $UO_2(NO_3)_2$ were refluxed with 30% TBP in dodecane for 5 days, and the system then reduced to one-third of its initial volume by distillation. The resulting organic layer was deep yellow in color and had a density of 1.44 g cm^{-3} (sample 1-23-5 in Tables 1 and 3). However, even this highly dense, concentrated organic phase still showed energetic behavior entirely consistent with $UO_2(NO_3)_2(TBP)_2$ being the major energy source — an exotherm at 234 °C (194 J g^{-1}) and an endotherm at 287 °C (130 J g^{-1}). A small exotherm was also observed at 256 °C (16 J g^{-1}), which may be due to the presence of a new energetic material.

During reflux reactions which employed cyclic hydrocarbon diluents, brown fumes of nitrogen oxides were almost always observed and the organic phases took on an orange or red color highly indicative of solvent nitration. DSC analysis of these phases revealed energetic behavior which differed somewhat from that of the $UO_2(NO_3)_2(TBP)_2$ adduct. Reflux of 4 M HNO$_3$/0.153 M $UO_2(NO_3)_2$ with 30% TBP in dodecane/1,2,4-trimethylcyclohexane (1:2) for 48 h produced a pale orange organic phase of density 1.18 g cm^{-3} (sample 1-14-3 in Tables 1 and 3). DSC analysis of this material revealed an exotherm at 174 °C (37 J g^{-1}), an exotherm at 270 °C (50 J g^{-1}) and an endotherm at 300 °C (46 J g^{-1}). Similarly, reflux of 6 M HNO$_3$/0.105 M $UO_2(NO_3)_2$ with 30% TBP in dodecane/hydrindane (1:1) for 72 h resulted in an orange organic phase of density 1.03 g cm^{-3} (sample 1-25-1 in Tables 1 and 3). This material showed an exotherm at 189 °C (75 J g^{-1}), an exotherm at 250 °C (15 J g^{-1}) and an endotherm at 291 °C (55 J g^{-1}). Thus the initial exothermic event in these systems occurred at a temperature between 30 and 50 °C *lower* than the exotherm due to $UO_2(NO_3)_2(TBP)_2$. Low-temperature exotherms were also exhibited by two 'red oil' samples which employed diluents containing hydrindane (exotherms at 189 °C and 180 °C, respectively), and one sample employing *n*-hexylcyclohexane (exotherm at 168 °C). Although the energy released in these exotherms is relatively small, this DSC evidence concurs with the belief that 'red oil' samples enter into exothermic decomposition reactions at temperatures substantially lower than that of the uranyl nitrate adduct $UO_2(NO_3)_2(TBP)_2$.

Since cyclic hydrocarbons are known to be more easily nitrated than dodecane, and since low temperature exothermic events were *only* observed in 'red oil' samples

Table 3
DSC behavior of 'red oil' samples in air

Sample	Density (g cm^{-3})	Energetic event	Temp. (°C)	Magnitude (J g^{-1})	Element analysis
1-7-1	1.25	Exotherm	233	126	C: 40.29% H: 8.10% N: 2.16%
1-7-3	—	Exotherm	234	53	C: 53.56% H: 9.97% N: 1.20%
1-9-1	1.01	Exotherm Endotherm	234 284	81 92	C: 57.35, 56.74% H: 10.60, 10.47% N: 1.56, 1.40%
1-9-2	1.04	Exotherm Exotherm Endotherm	225 258 304	22 8 75	C: 48.63% H: 8.45% N: 1.97%
1-9-3	108	Exotherm Exotherm Endotherm	176 247 302	5 78 52	C: 55.27% H: 9.37% N: 1.88%
1-14-1	1.02	Exotherm Exotherm Endotherm	182 249 296	8 94 39	—
1-14-3	1.18	Exotherm Exotherm Endotherm	174 270 300	37 50 46	C: 52.03, 50.90% H: 8.93, 10.07% N: 2.74, 2.40%
1-14-5	0.97	Exotherm Endotherm	230 302	115 52	—
1-20-1	1.07	Endotherm Exotherm Endotherm Exotherm	158 225 303 323	136 58 72 3	—
1-22-1	1.40	Exotherm Endotherm	233 294	278 124	C: 31.26% H: 4.69% N: 3.65%
1-23-2	1.30	Exotherm Endotherm	168, 231 304	267 97	C: 37.38% H: 6.32% N: 3.68%
1-23-5	1.44	Exotherm Exotherm Endotherm	234 256 287	194 16 130	C: 28.82% H: 5.37% N: 3.75%
1-25-1	1.03	Exotherm Exotherm Endotherm	189 250 291	75 15 55	C: 53.49% H: 9.95% N: 2.41%
1-26-1	—	Exotherm Endotherm	186, 250 294	128 15	C: 54.70, 55.38% H: 9.77, 9.98% N: 4.32, 3.68%
1-27-3	1.00	Exotherm Endotherm	180, 206 272 284	103 25	C: 57.05, 55.45% H: 10.54, 9.77% N: 3.33, 3.09%

Table 3 (continued)

Sample	Density (g cm^{-3})	Energetic event	Temp. (°C)	Magnitude (J g^{-1})	Element analysis
1-28-1	—	Exotherm	133	33	—
		Exotherm	235	411	
1-29-1	1.15	Exotherm	234	331	C: 52.99, 53.25%
					H: 8.52, 8.58%
					N: 5.20, 5.27%
1-31-2	1.08	Endotherm	70	11	C: 51.23, 51.09%
		Exotherm	246	160	H: 9.36, 8.46%
		Endotherm	290	7	N: 5.10, 4.67%
1-32-1	—	—	—	—	C: 46.43, 46.33%
					H: 8.10, 8.31%
					N: 5.46, 5.43%
DEC-39	1.09	Endotherm	63	118	—
		Exotherm	232, 257	206	
		Endotherm	284	81	
		Exotherm	318	11	
HYD-40	1.24	Exotherm	207, 265	190	C: 39.82, 40.77%
		Endotherm	297	79	H: 7.32, 6.92%
					N: 3.16, 3.23%
NAPH-41	1.28	Exotherm	197, 256	220	C: 38.51, 38, 67%
		Endotherm	299	69	H: 6.41, 6.70%
					N: 3.21, 3.37%
SPRAY-43	1.23	Exotherm	49	24	C: 42.91, 43.28%
		Exotherm	185, 255	162	H: 7.84, 8.08%
		Endotherm	310	51	N: 3.71, 3.58%
HYD-48	1.45	Exotherm	217, 265	197	C: 34.50, 33.81%
		Endotherm	300	94	H: 6.31, 6.04%
					N: 2.18, 2.13%

containing cyclic hydrocarbons, it is proposed that nitrated diluent materials may be responsible for these exothermic events. The energetic nature of nitrated hydrocarbons was shown by a DSC experiment performed on an organic sample containing highly-nitrated decalins (prepared by refluxing decalin with 10 M nitric acid). An exotherm of 947 J g^{-1} (226.3 cal g^{-1}) was observed on heating this sample from room temperature to 350 °C, with the first exotherm peaking at 172 °C. Two 'red oil' samples which employed decalin diluent during their preparation showed small exotherms at 176 °C and 182 °C, respectively – very similar to the decomposition temperature of the nitrated decalins themselves.

Total energy releases of the 'red oil' samples were $\leqslant$450 J g^{-1} (108 cal g^{-1}) in the temperature range studied, with a typical value for an 'average' material being 200 J g^{-1} (48 cal g^{-1}). To put this energy content into perspective, a typical explosive material such as RDX would show DSC exotherms of 1000 J g^{-1} or greater [28] and typical heats of explosion for selected energetic materials are: TNT 4564 J g^{-1} (1090 cal g^{-1}), nitroglycerine 6310 J g^{-1} (1507 cal g^{-1}) and picric acid 4396 J g^{-1} (1050 cal g^{-1}) [29].

The energy output of 100–450 J g^{-1} allows 'red oil' to be classified as an energetic material, but it is highly doubtful that it could be described as an explosive. In the presence of additional oxidant, and *especially* if the system is enclosed and heat loss is constrained, 'red oils' are capable of substantial, rapid releases of energy and gases, but as an *isolated* material in an open vessel the energetic content of the 'red oil' materials is best described as modest.

5. Discussion

The nature of the hydrocarbon diluent has been shown to play an important role in determining the color, density and energetic properties of the 'red oil' material produced, in agreement with earlier work [20]. A straight-chain hydrocarbon diluent, such as dodecane, always yielded an organic phase that was deep yellow in color and floated on the aqueous phase. Use of diluents containing a significant percentage of cyclic hydrocarbons, however, produced organic phases with colors ranging from yellow-orange to deep red, and phase inversions were observed in a number of cases. These observations are consistent with many previous studies investigating the effects of heating nitric acid with hydrocarbons [12–19, 30–55] which have shown that straight chain alkanes are most resistant to degradation, followed by branched chain alkanes, with cyclic alkanes being the species most susceptible to degradation [56].

Nitration of the diluent may also play a small but significant role in determining the density of the organic phase. Although the presence of a high concentration of uranium in the organic phase is the primary reason for its high density, an increase in density associated with nitration may be sufficient to cause a phase inversion. Thus reactions of diluent/TBP with HNO_3/$NaNO_2$ or HNO_3/HNO_2 mixtures at 60 °C for several hours have been shown to increase the organic phase density by 1.5–5% [15,30]. The formation of nitrated diluent species may also contribute to the energetic character of 'red oil'. In a recently reported DSC study of the effects of heating organic compounds, 113 out of 115 nitro compounds (R–NO_2) were found to undergo exothermic decomposition, as were 13 out of 15 nitroso (R–NO) compounds [57].

Observation of rapid overpressurizations in the bomb reactor at temperatures of ca. 125 °C is in agreement with previous work, in which vigorous reactions resulted from heating nitric acid, uranyl nitrate, sodium nitrate, sodium phosphate and TBP in a closed system at 120 °C [58] and also with a report that confinement of a 'red oil'/$UO_2(NO_3)_2$ mixture resulted in a more violent reaction upon heating [59]. The highly energetic results of heating nitrated organic materials in a sealed system have also been documented. When heated in a cell containing a pinhole opening, *iso*-amyl nitrite showed onset of decomposition at 159 °C and an exotherm of magnitude 137.0 cal g^{-1}, whereas in a sealed cell the onset temperature dropped to 109 °C and the energy release increased to 727.0 cal g^{-1} [57].

Reaction of nitric acid with TBP leads to successive formation of dibutyl- and monobutylphosphate (DBP and MBP, respectively) [60–65]. Furthermore, $UO_2(NO_3)_2$ will react with DBP at moderate temperatures to produce $UO_2(DBP)_2$ [60, 66, 67], which has been found to favor organic over aqueous phases and thus may

be present in 'red oil' samples [66]. Calorimetry studies on $UO_2(DBP)_2$ and the related $UO_2(HMBP)_2$, however, show that these molecules are *not* energetic – they undergo only endothermic decomposition. Thus the reaction of uranyl nitrate with degradation products of TBP leads only to compounds which are *less* energetic than $UO_2(NO_3)_2(TBP)_2$. $UO_2(NO_3)(DBP)(TBP)$ has been tentatively identified in 'red oil' materials [22], but the presence of only one nitrate ion per uranium implies a lower energy content per gram than $UO_2(NO_3)_2(TBP)_2$.

6. Conclusions

'Red oil' materials have been prepared which were felt to be representative of those found following the previously described [1] incidents at Hanford and Savannah River. Examination by differential scanning calorimetry showed that the materials enter into exothermic decomposition when heated to a sufficiently high temperature. The onset temperature of decomposition is dependent upon the nature of the hydrocarbon diluent employed during preparation of the 'red oil' sample. Use of straight-chain hydrocarbon diluents produces materials showing no exothermic behavior until the decomposition temperature of $UO_2(NO_3)_2(TBP)_2$ at ca. 220 °C. If the diluent contains a significant proportion of cyclic components, however, the 'red oil' material will often show a lower temperature exotherm at ca. 175 °C. The low temperature exotherm is proposed to be due to the presence of nitrated diluent components within the 'red oil' material, the presence of which has been established by infra-red and ^{13}C NMR spectra. The energy release of an isolated 'red oil' material upon heating in an *open vessel* is in the range 100–450 J g^{-1}, and is small compared to the energetic content of a typical explosive such as TNT as a result of the poor oxidant:fuel ratio within 'red oil'. Heating in sealed vessels, however, can result in sudden, extremely rapid release of gases and should be avoided even on a small scale.

7. Experimental details

Caution. Many of the experimental procedures involve heating nitric acid with organic materials at temperatures up to 145 °C. These procedures can be extremely dangerous due to the risk of explosive nitrate–organic reactions and must always be performed behind an adequate safety shield in a well-ventilated fume hood.

Tributylphosphate was shaken with aqueous sodium carbonate followed by deionized water, dried with anhydrous sodium carbonate and distilled under vacuum. Infra-red spectra were recorded on a Bio-Rad FTS40 instrument between KBr plates. Elemental analyses were performed by combustion in a Perkin-Elmer 2400 CHN analyzer. High-pressure reactions were carried out in a Parr 4563 stainless steel 600 ml mini-reactor, controlled by a Parr 4841 control unit. Differential scanning calorimetry and gas chromatography/mass spectrometry results were obtained by Monarch Analytical Laboratories, Maumee, OH. DSC results were obtained between room temperature and 350 °C at a heating rate of 10 °C/min. Temperatures given for

exothermic or endothermic reactions are the values for peak energy output, and not the onset temperature of reaction. Atmospheric pressure in Los Alamos is 590 Torr, and thus in some cases a mercury bubbler was used to bring the pressure within the flask to standard atmospheric (760 Torr).

7.1. Reflux procedure – sample 1-9-3

In a 1 l flask was placed 500 ml of an aqueous phase comprising 0.161 M $UO_2(NO_3)_2$ in 4 M nitric acid, and 100 ml of organic phase consisting of 30 ml of TBP, 44 ml of decalin and 26 ml of dodecane. The flask was attached to a 17 cm mercury bubbler and charged up to 760 Torr with argon. The flask contents were refluxed for 72 h and then allowed to cool. At the end of the reaction a deep orange organic phase was observed which was collected using a teat pipette. The density of this sample was 1.08 g cm^{-3}. Analysis: C, 55.27; H, 9.37; N, 1.88%. DSC (air): Exotherm 5 J g^{-1} at 176 °C; exotherm 78 J g^{-1} at 247 °C; endotherm 52 J g^{-1} at 302 °C. IR (liquid film, KBr plates): 1766 (w), 1728 (m), 1660 (s), 1553 (m), 1536 (sh, m), 1459 (sh, m), 1449 (m), 1384 (s), 1269 (m), 1220 (m), 1184 (s), 1036 (s), 939 (m), 824 (w), 792 (w), 736 (w), 537 (w), 470 (w).

7.2. Reflux/distillation procedure – sample 1-22-1

In a 1 l flask was placed 300 ml of an aqueous phase comprising 0.312 M $UO_2(NO_3)_2$ in 6 M nitric acid, and 50 ml of organic phase consisting of 15 ml of TBP, 22 ml of decalin and 13 ml of dodecane. The flask contents were refluxed for 72 h to give an orange organic phase floating on the aqueous phase. The apparatus was then changed to a distillation configuration and 225 ml of distillate collected before the flask was allowed to cool. A deep orange organic layer was seen to be floating on a yellow aqueous phase. Density of this sample was 1.40 g cm^{-3}, while that of the aqueous phase was 1.50 g cm^{-3}. Analysis: C, 31.26; H, 4.69; N, 3.65%. DSC (air): Exotherm 278 J g^{-1} at 233 °C; endotherm 124 J g^{-1} at 294 °C. IR (liquid film, KBr plates): 2401 (m), 1828 (m), 1765 (m), 1664 (w), 1528 (m), 1390 (s), 1269 (m), 1213 (sh, m), 1172 (m), 1039 (s), 936 (m), 828 (m), 748 (w).

7.3. High-pressure bomb procedure – sample 1-29-1

Into the Parr reactor was placed 250 ml of an aqueous phase comprising 0.10 M $UO_2(NO_3)_2$ in 4 M nitric acid, and 50 ml of organic phase consisting of 15 ml of TBP and 35 ml of Shell Spray Base. The bomb was sealed, stirring was switched on and the bomb contents heated to 94 °C, where the temperature was held for 10 hours (pressure rose to 220 psi). Temperature was increased in increments of 5 °C until the bomb contents had reached 141 °C (720 psi), and held at this temperature for 10 min before being allowed to cool. When the contents were poured into a beaker, a deep orange organic phase was seen to sink beneath the yellow aqueous phase. Density of this sample was 1.15 g cm^{-3}. Analysis: C, 52.99, 53.25; H, 8.52, 8.58; N, 5.20, 5.27%. DSC (air): Exotherm 331 J g^{-1} at 234 °C. IR (liquid film, KBr plates): 2396 (w), 1760

(sh, w), 1721 (br, s), 1661 (m), 1628 (m), 1550 (br, s), 1458 (s), 1383 (s), 1221 (m), 1174 (s), 1120 (w), 1029 (s), 957 (w), 932 (m), 913 (w), 849 (w), 823 (w), 773 (w), 737 (w), 546 (w), 467 (w).

References

[1] (a) D.O. Campbell and J.C. Mailen, The Red-oil Problem and its Impact on Purex Safety, ORNL/TM-10798, Oak Ridge National Laboratory, 1988; (b) J.G. Watkin, The 'Red Oil' Problem— History, Chemistry and Relevance to Hanford Waste Tank Safety Concerns, LAUR-92-3168 Rev. 1, Los Alamos National Laboratory, 1992.

[2] R.E. Tomlinson, Unusual Incident at Savannah River, HW-27122, Hanford Works, February 1953.

[3] L.W. Gray, An explosion and fire during conversion of liquid uranyl nitrate to solid uranium oxide, Nucl. Safety, 19 (1978) 91.

[4] J.M. McKibben, Explosion and Fire in the Uranium Trioxide Production Facilities at the Savannah River Plant on February 12, 1975, DPSPU 76-11-1, Savannah River Plant, October 1976.

[5] W.S. Durant, Red Oil Explosions at the Savannah River Plant, DP-MS-83-142, Savannah River Laboratory, 1983.

[6] G. Sege, Overconcentration in Initial Operation of Uranium Evaporator – 321 Building, HW-28690, Hanford Atomic Products Operation, July 1953.

[7] N.J. James and G.T. Sheppard, Red oil hazards in nuclear fuel reprocessing, Nucl. Eng. Design, 130 (1991) 59.

[8] T.J. Colven Jr., G.M. Nichols and T.H. Siddall, TNX Evaporator Incident January 12, 1953, DP-25, Savannah River Laboratory, May 1953.

[9] W.S. Durant, L.W. Gray, R.M. Wallace and W.W.F. Yau, Explosions and other Uncontrolled Chemical Reactions at Non-nuclear Facilities of the Savannah River Plant, DP-MS-88-15, Savannah River Laboratory, 1988.

[10] M.H. Curtis, TBP Process Investigation – Formation of 'Red Oil' in Extraction Column Studies, HW-19997-RD, Hanford Atomic Products Operation, January 1951.

[11] W.C. Perkins, W.S. Durant and M.L. Hyder, The Safety of UO_3 Production in the A-line at the Savannah River Plant, DP-1449, Savannah River Laboratory, March 1977.

[12] B.P. Dennis, Radiolytic and Chemical Stability of Pure Hydrocarbons, DP-577, Savannah River Laboratory, April 1961.

[13] R.M. Wagner, Nitration Reactions of Shell Spray Base under Purex Waste Recovery Process Conditions, HW-26517, Hanford Works, December 1952.

[14] R.H. Moore, Chemical Stability of Purex and Uranium Recovery Process Solvent, HW-34501, Hanford Atomic Products Operation, March 1955.

[15] J.E. Mendel, Use Test Comparison of TBP Diluents, HW-70199, Hanford Atomic Products Operation, July 1961.

[16] K.B. Brown, Chemical Technology Division, Chemical Development Section C, Progress Report for June–July 1960, ORNL-CF-60-7-108, Oak Ridge National Laboratory, September 1960.

[17] K.B. Brown, K.A. Allen, C.A. Blake, C.F. Coleman, D.J. Crouse and A.T. Gresky, Chemical Technology Division, Chemical Development Section C, Monthly Progress Report, November 1959, ORNL-CF-59-11-132, Oak Ridge National Laboratory, January 1960.

[18] H. Pollock, A Stable Diluent for Purex Process Extractants, DP-294, Savannah River Laboratory, June 1958.

[19] E.S. Lane, Performance and degradation of diluents for TBP and the cleanup of degraded solvents, Nucl. Sci. Eng., 17 (1963) 620.

[20] R.G. Wilbourn, Safety Aspects of Solvent Nitration in HTGR Fuel Reprocessing, GA-A14372, General Atomic, June 1977.

[21] R.M. Wagner, Investigation of Explosive Characteristics of Purex Solvent Decomposition Products (Red Oil), HW-27492, Hanford Works, Mar. 1953.

[22] L. Stieglitz, R. Becker, H. Bautz and R. Will, Properties of heavy organic phases and their formation in the purex process, Proc. Int. Solv. Extr. Conf., Vol. 1, Munich, FRG, 1986, pp. 239–244.

[23] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, 5th edn., Wiley, New York, 1991.

[24] R.J. Lewis Sr., Hazardous Chemicals Desk Reference, 2nd edn, Van Nostrand Reinhold, New York, 1991.

[25] N.I. Sax and R.J. Lewis Sr., Dangerous Properties of Industrial Materials, 7th edn., Van Nostrand Reinhold, New York, 1989.

[26] T.C. Runion and C.V. Ellison, TBP Process for Uranium Recovery from Metal Waste – Laboratory Summary, ORNL-557, Oak Ridge National Laboratory, January 1950.

[27] W.H. Baldwin, W.E. Clark and W.B. Howerton, Synthesis of Aliphatic Nitrate Esters by Reaction of Metal Nitrates with Phosphate Esters, ORNL/TM-6736, Oak Ridge National Laboratory, March 1979.

[28] S.M. Shen, A.L. Leu and H.C. Yeh, Evaluation method for the effect of salts on the elimination of secondary flames of energetic materials by differential scanning calorimetry, Thermochim. Acta, 177 (1991) 23.

[29] R. Meyer, Explosives, 3rd ed., VCH, Weinheim, 1987.

[30] R.K. Klopfenstein, Studies of the Behavior of the TBP-Kerosene Solvent in Uranium Refining: Degradation of the Kerosene Diluent, NLCO-769, National Lead Company of Ohio, May 1959.

[31] O.K. Tallent, J.C. Mailen and K.D. Pannell, Purex Diluent Degradation, ORNL/TM-8814, Oak Ridge National Laboratory, February 1984.

[32] Chemical Technology Division, Chemical Development Section C, Progress Report for August–September 1961, ORNL-TM-27, Oak Ridge National Laboratory, December 1961.

[33] R.H. Moore, Investigation of Solvent Degradation Products in Recycled Uranium Recovery Plant Solvent, HW-34502 REV, Hanford Atomic Products Operation, April 1955.

[34] H.E. Shook Jr., Solvent Degradation Products in Nuclear Fuel Reprocessing Solvents, DP-1759, Savannah River Laboratory, June 1988.

[35] H.E. Shook Jr., Analysis of Residual Organic Materials in Aqueous Radioactive Streams from the Purex Process, DP-1744, Savannah River Laboratory, May 1987.

[36] R.H. Ellerhorst and R.K. Klopfenstein, Literature Search: TBP-Kerosene Solvent Degradation, NLCO-744, National Lead Company of Ohio, February 1958.

[37] W.H. Baldwin, Nitrohydrocarbon from the Reaction between Amsco and Nitric Acid, ORNL-59-11-66, Oak Ridge National Laboratory, November 1959.

[38] R.A. Pugh, Notes Pertaining to Recuplex Product Evaporation, HW-32100, Hanford Atomic Products Operation, April 1954.

[39] D.A. Orth, Purex: Process and Equipment Performance, DP-MS-86-28, Savannah River Laboratory, 1986.

[40] D.A. Orth and T.W. Olcott, Purex process performance versus solvent exposure and treatment, Nucl. Sci. Eng., 17 (1963) 593.

[41] C.A. Blake Jr., W. Davis Jr. and J.M. Schmitt, Properties of degraded TBP-Amsco solutions and alternative extractant-diluent systems, Nucl. Sci. Eng., 17 (1963) 626.

[42] A.J. Huggard and B.F. Warner, Investigations to determine the extent of degradation of TBP/odorless kerosene solvent in the new separation plant – Windscale, Nucl. Sci. Eng., 17 (1963) 638.

[43] Z. Nowak and M. Nowak, Radiolytic and thermal degradation of dodecane – 30% TBP – HNO_3 systems, Radiochem. Radioanal. Lett., 14 (1973) 161.

[44] Z. Nowak and M. Nowak, Thermal degradation of TBP–diluent systems, Radiochem. Radioanal. Lett., 38 (1979) 377.

[45] R. El Bacha, J. Cressely, C. Tanielian and S. Libs, Nitration of Methylcyclohexane – I, Nitration in the liquid phase by nitric acid, Bull. Soc. Chim. Fr., (1974) 1053.

[46] J. Cressely, C. Tanielian and A. Ulrich, Nitration of decalin–III, 9-Nitrodecalin obtained by liquid phase nitration, Bull. Soc. Chim. Fr., (1973) 1090.

[47] J. Cressely, C. Tanielian and A. Ulrich, Nitration of decalin–II, comparison of nitration of *cis-* and *trans-*decalins in the liquid phase, Bull. Soc. Chim. Fr., (1973) 1087.

[48] J. Cressely, C. Tanielian and A. Ulrich, Nitration of decalin – IV, secondary nitro derivatives obtained from *trans*-decalin, Bull. Soc. Chim. Fr., (1973) 1095.

[49] O.F. Hill and F.J. Leitz, Progress Report for September 1950 – Chemical Research Section, HW-19155, Hanford Works, October 1950.

[50] J.L. Swanson, The Stability of Purex Solvent to Radiation and Chemical Attack, HW-38263, Hanford Atomic Products Operation, May 1955.

[51] W.K. Eister, Chemical Technology Division, Progress Report for the Quarter Ending May 31, 1950, ORNL-763, Oak Ridge National Laboratory, July 1950.

[52] K.J. Ohwada, Group type analysis of carboxylic acids formed by degradation of *i*-dodecane and kerosene with nitric acid, Nucl. Sci. Technol., 4 (1967) 427.

[53] T. Ishihara and K.J. Ohwada, On fission product retention of degraded kerosene with nitric acid, Nucl. Sci. Technol., 3 (1966) 243.

[54] T. Ishihara and K.J. Ohwada, Chemical degradation of kerosene diluent with nitric acid, Nucl. Sci. Technol., 3 (1966) 20.

[55] K.J. Ohwada, On the identification of hydroxamic acids formed by nitric acid degradation of kerosene and *i*-dodecane, Nucl. Sci. Technol., 5 (1968) 163.

[56] C. Ellis, The Chemistry of Petroleum Derivatives, 1st edn., Chemical Catalog Co., New York, 1934.

[57] T. Ando, Y. Fujimoto and S. Morisaki, Analysis of differential scanning calorimetric data for reactive chemicals, J. Hazard. Mater., 28 (1991) 251.

[58] T.H. Siddall, Laboratory Investigation of Exothermic Reactions of Organic-Aqueous Mixtures Encountered in the Purex Process, DPST-53-41-4, Savannah River Laboratory, July 1953.

[59] J.J. Shefcik, Safety Aspects of Purex Plant Concentrator Operation, HW-40556, Hanford Works, December 1955.

[60] R.M. Wagner, Hydrolysis Products of Tributylphosphate and their Effect on the Tributylphosphate Process for Uranium Recovery, HW-19959, Hanford Works, April 1951.

[61] E.K. Dukes, The Formation and Effects of Dibutylphosphate in Solvent Extraction, DP-250, Savannah River Laboratory, November 1957.

[62] W.W. Morgan, W.G. Mathers and R.G. Hart, Processing of irradiated reactor fuels, Ind. Eng. Chem., 51 (1958) 817.

[63] L.L. Burger and E.D. McClanahan, Tributyl phosphate and its diluent systems, Ind. Eng. Chem., 50 (1958) 153.

[64] R.H. Ellerhorst, Studies of the Behavior of the TBP-Kerosene Solvent in Uranium Refining: Recovery of Discarded Refinery Solvent, NLCO-714, National Lead Company of Ohio, January 1958.

[65] W. Davis Jr. and A.H. Kibbey, Aqueous-Phase Decomposition of Tributylphosphate at 35 °C to 75 °C in Nitric Acid Solutions, ORNL-TM-3062, Oak Ridge National Laboratory, August 1970.

[66] H.T. Hahn and E.M. Vander Wall, TBP decomposition product behavior in post-extractive operations, Nucl. Sci. Eng., 17 (1963) 613.

[67] J.H. Burns, Solvent extraction complexes of the uranyl ion – 2, Inorg. Chem., 22 (1983) 1174.