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REVIEW

Decomposition of Solvent Extraction Media during Nuclear Reprocessing: Literature Review

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ABSTRACT

Reprocessing spent nuclear fuel is indispensable for the economical use of uranium in nuclear energy production, and has been used industrially for more than 40 years. These processes involve the use of an extractant/diluent (solvent) for separation of the reusable actinides from unwanted fission products. The most widely used processes employ tributyl phosphate (TBP) diluted with normal-paraffin hydrocarbon. However, on repeated use, the solvent becomes degraded due to thermal, radiolytic, and chemical attacks, resulting in chemical as well as physical damage. In view of the considerable expansion in the knowledge and understanding regarding the chemical and radiolytical decomposition of both TBP and the hydrocarbon diluent, an up-to-date review seemed appropriate. This review is concerned mainly with the mechanisms of the degradation of the solvent system. Schemes of TBP and diluent radiation-chemical transformations occurring on decomposition of the solvent system are presented.

Key Words. Purex process; Radiolysis; Solvent extraction; Degradation; Decomposition; TBP

INTRODUCTION

The subject of the stability of solvent-extraction systems has been reviewed several times in the past (1–7). The most recent general review concerning solvent extraction was published in 1984 (7). It covered all aspects relevant to the chemistry, chemical technology, and engineering of solvent-extraction processes using TBP as the extractant (7). In view of the considerable expansion in the knowledge and understanding regarding solvent degradation, an up-to-date review is appropriate. This present review focuses mainly on diluent degradation; TBP decomposition will receive little attention as this subject has been reviewed adequately elsewhere (8–21).

Nuclear Fuel Solvent Extraction Processing

General Introduction

The use of tributyl phosphate (TBP) in an organic diluent as an extractant during the reprocessing of nuclear fuels is well established. However, the main drawbacks of these solvent systems are their failure to decontaminate the actinides effectively from fission products, principally ruthenium, zirconium, cerium, and niobium. The other main defect is the solvent susceptibility to both chemical and radiolytic degradation.

A consequence of these defects is that the operation of nuclear fuel reprocessing plants is affected. Several solvent extraction cycles, each involving extraction, scrub, and stripping stages, are necessary to obtain the actinides sufficiently free of the fission products to enable their reuse in the complete fuel cycle. Moreover, in order to recycle the solvent continuously in the reprocessing plant, it must be cleaned of the degradation products after it has passed through the plant by a washing process prior to its reuse. However, degradation products of the diluent are less easily removed by the classical alkali wash procedure, in contrast to the degradation products of TBP.

Effects of Solvent Degradation on Reprocessing

The reduced performance of the solvent is not entirely caused by the formation of degradation products of TBP and their possible complexing with heavy metals and fission products (22–24). The second component of the solvent used during the extraction process, the diluent, may also be prone to degradation under the influence of radiation or at elevated temperatures (25–27). Unlike the decomposition products of TBP, these degradation products are not removed by aqueous alkalies in the solvent wash systems, but slowly accumulate and reduce the performance of the solvent. This is demonstrated by poor phase separation, decreased mass transfer coefficients for uranium and plutonium, and retention of fission products in the uranium and plutonium product streams among many others (28–34).

The degradation chemistry is extremely complex. The extent to which degradation occurs and the nature of the degradation products obtained are known to vary with the type of diluent employed (35). It is well established (36) that the order of susceptibility of hydrocarbons to thermal and radiolytic attack is olefins > naphthenes > isoparaffins > *n*-paraffins (37). Odorless kerosene (OK) is shown to be a fairly suitable diluent but is less stable than pure branched and straight chain hydrocarbons such as *n*-dodecane. The comparisons of diluents by different workers have produced confusing results because of the multiplicity of performance tests used for evaluation.

Degradation Products of Diluents and Their Complexing Ability

According to some workers (38, 39), thermal degradation in the presence of nitric acid and nitrous acid gives a similar reduction of diluent performance to that due to radiolytic degradation. The species mainly involved in the thermal degradation of the diluent was thought to be nitrous acid (40), since an induction period is involved in its formation. However, the principal impurities originating from the diluent positively identified are likely to be:

- Aliphatic nitro compounds, which result from nitration by nitric or nitrous acids.
- Aliphatic carboxylic acids, resulting from oxidation reactions of nitric and nitrous acids.
- Aliphatic nitroso compounds, produced by the action of nitrous acid on secondary nitro compounds.
- Aromatic compounds, probably nitro and nitroso derivatives.
- Ketones and aldehydes which may be intermediates in oxidation reactions leading to carboxylic acids formation.

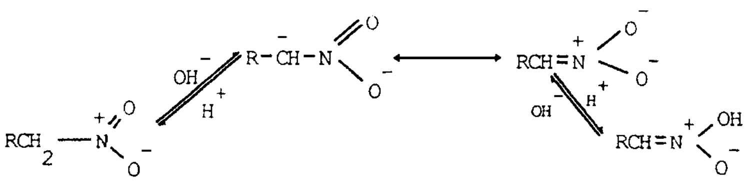
The principal decomposition products originating from TBP would simply be:

- Dibutyl phosphate (HDBP) resulting from hydrolysis of TBP.
- Additional phosphorus compounds.

The long-term deterioration of the solvent is ascribed to the degradation products from the diluent, since they are not removed by alkaline wash from the organic phase. The nitro compounds may be offensive only in that being chemically very reactive; their presence results in formation of secondary reaction products having much worse characteristics.

Lane's Hypothesis

Lane (41) and Huggard and Warner (42), adopting as a base the well-known Meyer and Nef reactions (43, 44), suggested that the main complexing species from diluent degradation in the presence of nitric acid were hydroxamic acids, RCONHOH; the precursors to these complexing species were postulated as primary nitroparaffins formed by either nitration of the —CH_3 groups in hydrocarbons in hydrocarbon chains, nitration of alkyl side chains in aromatic and naphthenic compounds, nitration of terminal ethylenic linkages in olefins, or the ring opening of naphthenic compounds. These primary nitroparaffins can react in a number of different ways depending upon the solution characteristics, and these can be illustrated by first considering the isomeric forms of the nitroparaffin.



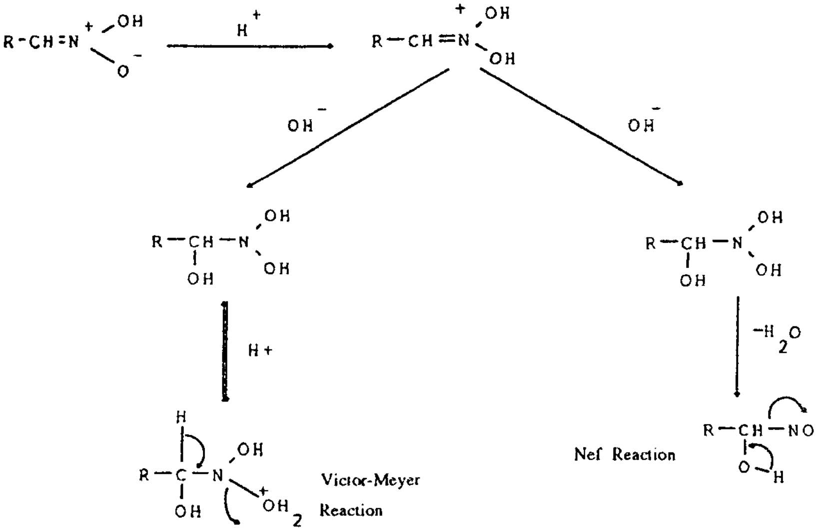
Nitro-form

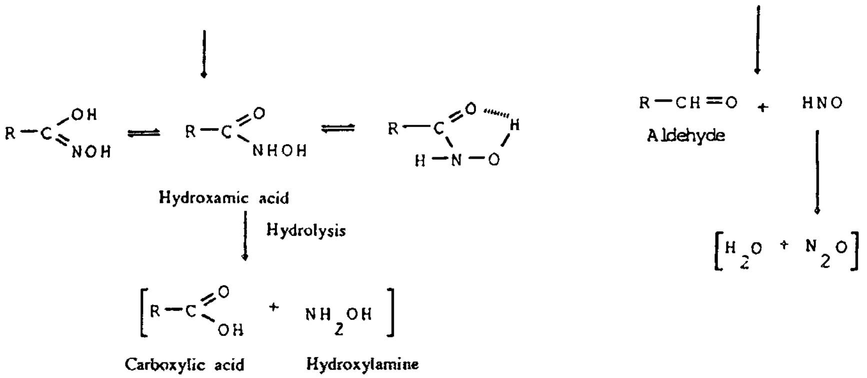
(Nitroparaffin)

Aci-form

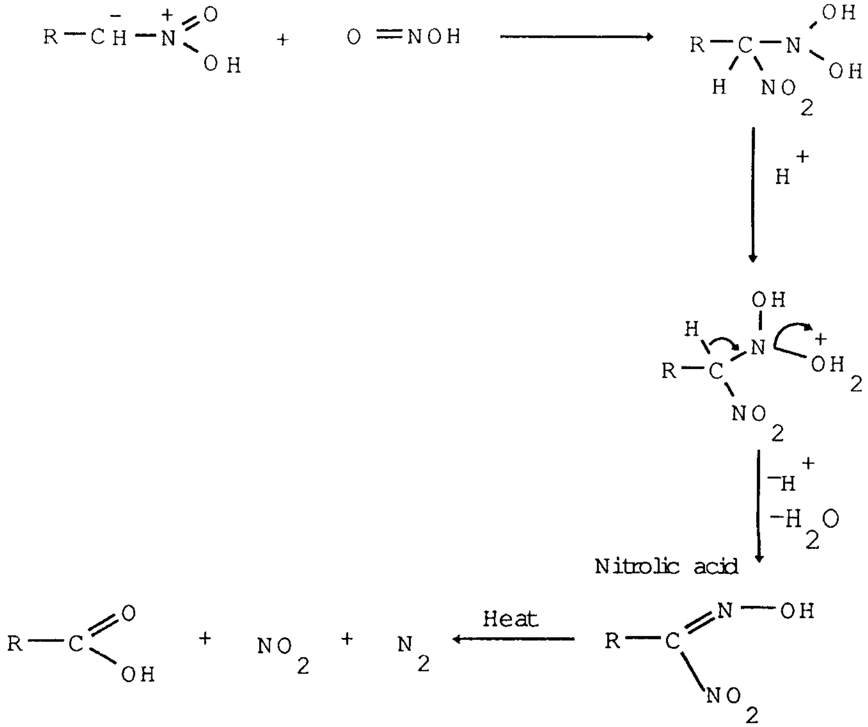
(Nitronic acid)

Subsequent reaction of the aci-form can be considered following acidification via:





Both hydroxamic acids and nitronic acids are capable of complexing with metallic ions, which could be of major importance if degraded species are not removed from the solvent. In addition, nitrous acid can react with one of the above isomeric species as below:



The nitrolic acids are colorless or faintly yellow compounds which are soluble in water and organic solvents. However, in excess alkali they produce an intense red color caused by the formation of a soluble red-colored salt of a nitrolic acid, and these crystallize very well and are extremely explosive substances.

It has been reported that a dodecyl hydroxamic acid–ferric iron complex had been observed in a degraded solvent containing added iron but that otherwise no hydroxamic acids had been isolated (45). Lane (41) concluded that the addition of primary nitro compounds did not produce metal retention until a substantial concentration of hydroxamic acid built up by the mechanism specified above. Hydroxamic acids do accumulate but are lost from the system by hydrolysis. Further prolonged alkali washing can increase the steady-state concentration of the aci-form of the nitroparaffin, which can react as outlined by Lane (41).

Support for the former hypothesis comes from an extraction test (42) with 20% TBP–OK solvents containing laurohydroxamic acid and from the subsequent studies (46) with benzohydroxamic acid in nitric acid solutions. In both cases it has been shown that hydroxamic acids have a highly specific complexing action for zirconium and that the complexes are very stable and not easily removed from the organic phase. This effect was not present if other substances such as oximes or nitrolic acid were substituted.

In addition, positive identification of hydroxamic acids formed by nitric acid degradation of both isododecane and OK was confirmed by other workers (47), who noted their presence by the classical ferric chloride test and various spectroscopic techniques as well as by extraction of fission products and zirconium nitrate. This was further supported by an examination of the chemical behavior of model long-chain alkyl hydroxamic acids.

In an attempt to test whether hydroxamic acids are responsible for metal retention in recycled solvent, Healy et al. (48) synthesized a number of hydroxamic acids and examined their behavior in HNO_3/TBP/OK systems, and in particular the effect of laurohydroxamic acid. In order to do this, they developed a more sensitive colorimetric method from a vanadium spot test for detection of hydroxamic acids (49). The detection limits of this method are of the order of 5×10^{-6} M, and the method is not affected by the presence of either zirconium or uranium. In contrast, the ferric chloride test has a detection limit of about 2×10^{-4} M, and the determination is strongly affected by the presence of zirconium and uranium. Their findings indicated that concentrations of the order of 10^{-4} to 10^{-3} M laurohydroxamic acid can lead to strong metal retention in solvent mixtures, and laurohydroxamic acid has a much greater effect than HDBP.

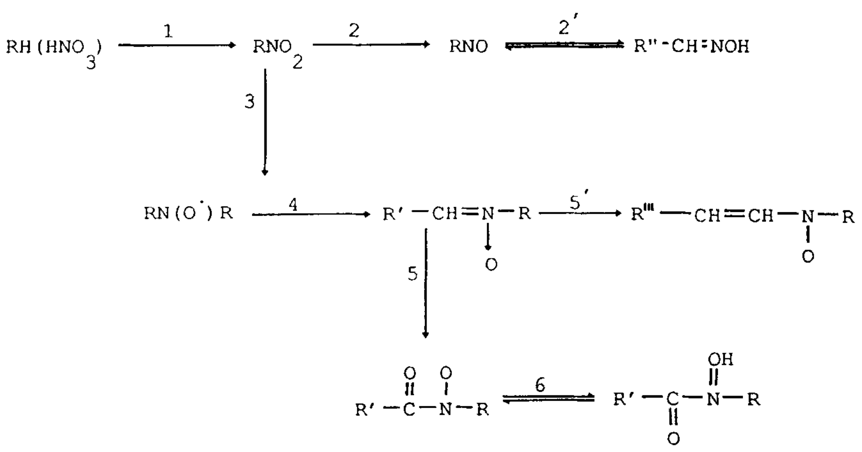
The effect of nitrous acid on hydroxamic acid was also studied, and it was found that contacting laurohydroxamic acid in TBP/OK with nitrous acid in 0.5 M HNO_3, 1 mole of nitrous acid is required to destroy (by oxidation) 1 mole of laurohydroxamic acid, as in Eq. (1). At higher acidity, 4 moles of laurohydroxamic acid are destroyed by 1 mole of nitrous acid as illustrated in Eq. (2).

$$RCONHOH + HNO_2 \rightarrow RCOOH + N_2O + H_2O \qquad (1)$$

$$4RCONHOH + HNO_2 + HNO_3 \rightarrow 4RCOOH + 2N_2O + H_2O \qquad (2)$$

The question of the stability of hydroxamic acid was also reviewed by Nowak et al. (50). They observed the formation of hydroxamic acid at nitric acid concentration less than 1 M, whereas at higher nitric acid concentrations the large amount of nitrous acid formed during radiolysis of the solvent system prevented the authors from detecting hydroxamic acids. They also suggested that hydroxamic acids were destroyed by nitrous acid.

A kinetic study (51) for a model system comprising the conversion of 1-nitropropane to propanhydroxamic acid, and the subsequent hydrolysis to carboxylic acid and hydroxylamine, indicated that the mechanism suggested earlier, if it applies (52, 53), means that the most favorable conditions would give stationary hydroxamic acid concentrations not exceeding 10^{-7} mol/L, which is clearly insufficient to explain the selective deterioration in solvent extraction. It is also assumed that the hydroxamic acids are formed only in the aqueous phase, explaining the extremely low calculated hydroxamic acid concentrations for the primary nitro compounds considered.

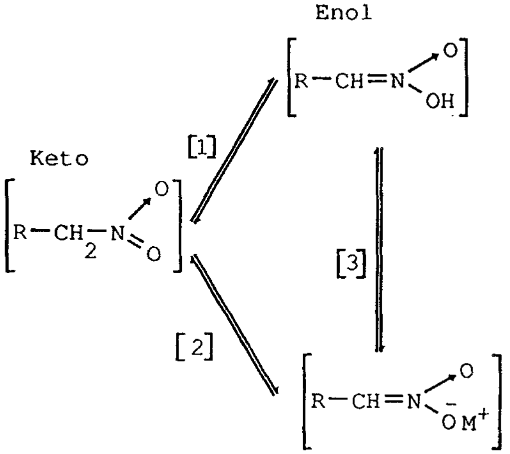


Conversely, recently published research (54), in which a mixture consisting of TBP and normal dodecane were irradiated in the presence of nitric acid, revealed that the steady-state hydroxamic acid concentrations in the organic phase were found to be much higher than previously calculated (51). As a result, the authors deduced that a radiolytic mechanism was operating directly in the organic phase. They assumed that the nitration of the radiolytic degradation products of both the extractant and the diluent give rise to reactions producing hydroxamic acids.

In contrast to the data previously mentioned, several new features have come to light recently (23). First, the concentration of hydroxamic acid in the irradiated solvent was found to be 4.4 × 10^{-4} M, 1000 times greater than previously reported. Second, the nitrous acid could not totally destroy hydroxamic acid if the uranium concentration in the aqueous phase was high (i.e., 30 g/L), and finally the ruthenium retention increases with the hydroxamic acid concentrations.

Blake's Hypothesis

In contrast to Lane (41), Blake et al. (55) concluded that the presence of nitroparaffins in the enol form were the main metal complexing species, possibly as a result of a synergistic extraction in the presence of TBP. The following equilibria were postulated:

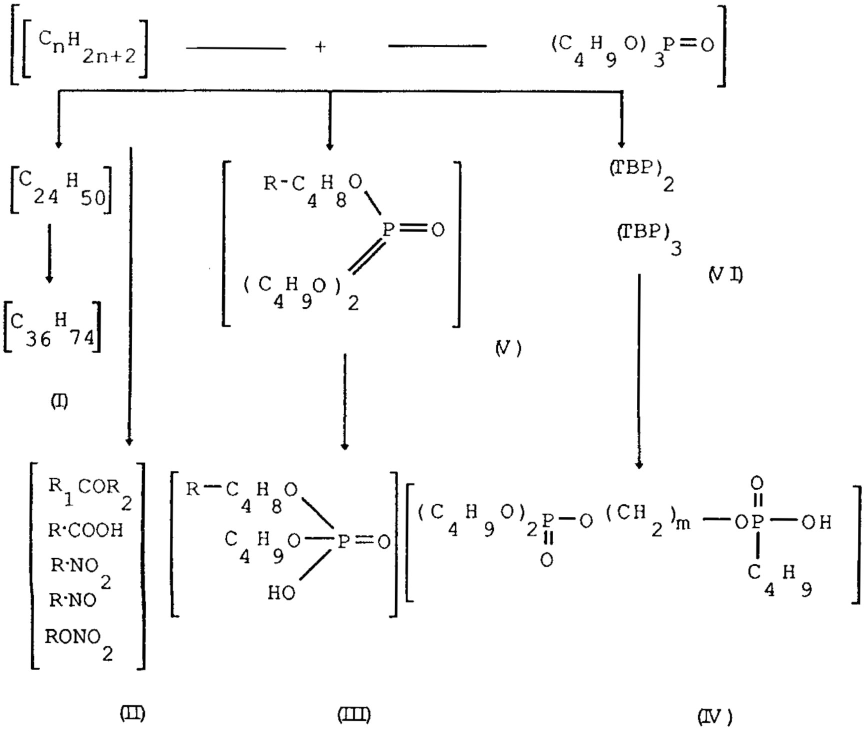


In acid conditions the equilibrium of Reaction [1] favors the keto form and equilibrium is slow, whereas the equilibrium of Reaction [2] in basic media favors the enol form and equilibration is moderately fast. Change to an acid medium, however, produces the free enol form in a much larger amount than via Reaction [1], and the hydroxamic acid may then in turn form metal complexes. Despite the different reaction mechanisms postulated to account for the metal retention by diluent degradation product production, all these groups of workers indicated that the elimination of nitroparaffins during solvent washing was desirable.

On the second theory, Baroncelli et al. (56) noted that aci-nitroparaffins are unstable in nitric acid solutions even at room temperature. Therefore it seems that complexing with hydroxamic acids is a more likely mechanism for zirconium retention. In any case, both mechanisms indicate that the removal of nitroparaffins from the system should reduce the complexing action of diluent degradation products with fission products.

Becker's Hypothesis

By far the most comprehensive investigation of the radiolytic and chemical behavior of the TBP–dodecane–nitric acid system was carried out by Stieglitz and coworkers (57–59). Using a combination of gas chromatography–mass spectroscopy, they characterize in excess of 20 degradation products with molecular weights ranging from 238 to 365. Most of these were attributed to acid phosphate esters. As a result of their findings, a reaction scheme has been suggested:



Oligomers of dodecane form Class I. Class II comprises ketones, aliphatic acids, nitroalkanes, nitroso compounds, and nitrate esters. These degradation products offer variable carbon chain lengths, and they result from the reaction between organic alkyl radicals from the diluent and inorganic radicals such as OH, NO, and O_2. No negative effects on process performance through metal formation and fission products retention were associated with these primary degradation products. However, a gradual deterioration in the physicochemical properties of the solvent was observed with time.

In addition they dismissed the suggestion of hydroxamic acids formation by rearrangement reactions involving nitro compounds since the presence of the hydroxamic acid had never actually been confirmed by chemical analysis. Infrared analysis of the residues resulting from intensive solvent concentration and separation involving high-vacuum molecular distillation and column chromatography indicated the presence of the two compound Classes III and IV. These compounds exhibit high extraction properties toward tetravalent metals.

Over 18 long-chain acid phosphates have been identified. These compounds, which are included in Class III, are formed by a combination of alkyl radicals from TBP ranging from C_2H_5 to $C_{12}H_{25}$, following the elimination of a butyl group or directly from HDBP.

Class IV consists of 11 isomers of an acid dimeric TBP, which were isolated and eventually characterized. Again these compounds show a high affinity for tetravalent metals because of the presence of the acid phosphate groups.

The presence of Class VI oligomeric butyl phosphate with molecular weights of 530, 800, and 1005 was demonstrated. This was confirmed using gas chromatographic and gel chromatographic techniques. As a result it was concluded that Class IV type molecules were produced by the recombination of alkyl and TBP radicals. Therefore, it can be deduced that the radiolytic attack initially produces smaller molecules which subsequently recombine to yield larger species. Support for this hypothesis came from the presence of compounds of Classes I, III, IV, and VI.

Classes III and IV type molecules include acid phosphate esters. The chemistry of these compounds is easily explained by comparison with HDBP and, in fact, stable complexes are obtained with tetravalent metals such as zirconium, uranium, and plutonium with these compounds. Moreover, due to the presence of much longer alkyl groups, the solubility of the sodium salts (formed during the alkali washing of the solvent) of these two classes of compounds in the organic phase is high, inferring that accumulation occurs with solvent recycle. Furthermore, the above-mentioned compounds are interfacially active and are capable of forming emulsions at the interface in the solvent contactors with all the problems this implies—frothing, fission product accumulation, and loss of interface control.

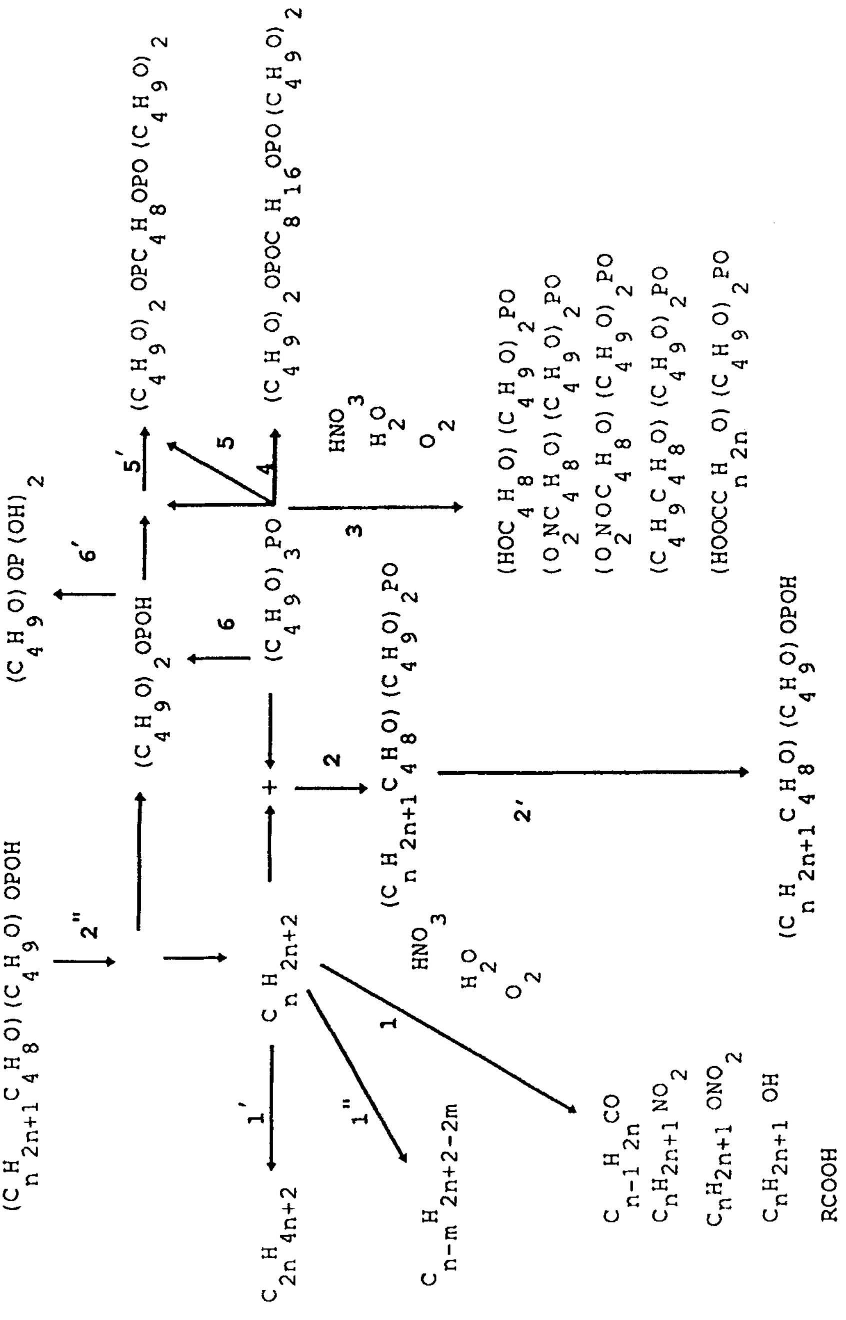
Adamov's Hypothesis

More recently, Adamov and coworkers (60–62) proposed a more complete picture of radiation and chemical transformations of both TBP and hydrocarbon diluent in the reprocessing plant. Using purely chromatographic techniques for preliminary separation, and mass spectroscopy for characterization, it proved possible to separate the majority of constituent products into distinct groups. They therefore proposed an overall reactions scheme (see page 2614).

The majority of decomposition products resulted from nitration and oxidation of both TBP and hydrocarbon diluents, as illustrated in the scheme by reaction Routes **3** and **1**, respectively. These nitration and oxidation reactions arise from the actions of HNO_3, O_2, H_2O, and their radiolysis products on the organic components.

Further radiolysis products were characterized. These included dimers of TBP (Route **4**), and hydrocarbon diluent (Route **1′**). These most probably resulted from radical recombinations which occurred alongside condensation reactions (Route **5**) and (Route **1″**), producing species with molecular weights lower than the dimers. Radical recombinations involving alkyl and TBP radicals yielded mixed compounds, such as alkyl dibutylphosphate (Route **2**), which then underwent hydrolysis by hydroxyl (Route **2′**). TBP itself underwent hydrolysis to yield HDBP (Route **6**), which in turn underwent further hydrolysis (Route **6′**) as well as radical combinations with TBP (Route **5′**) and with hydrocarbon diluent (Route **2″**).

Adamov attempted to determine which particular degradation process had the greatest influence on the decomposition, such as radiation damage or purely chemical attack, or a combination of both. This was achieved by examining irradiated samples containing an increasing number of constituents ranging from TBP–H_2O to the TBP–H_2O–HNO_3–tridecane system. In TBP–HNO_3, Routes **1** and **3**, the nitrations and oxidations predominated, while in TBP–H_2O, Routes **4** and **5**, the dimerization and condensation involving TBP, were the main reactions. In TBP–H_2O–tridecane, Route **2**, the condensation reaction involving TBP and tridecane prevailed. Finally, in the system consisting of TBP–H_2O–HNO_3–tridecane oxidation, reaction Route **3** occurs alongside TBP condensation with tridecane. The predominance of one degradation process over another is determined by the composition of the extraction system.


(CnH2n+1C4H8O)(C4H9O)OPOH
(C4H9O)OP(OH)2
(C4H9O)2OPOH
(C4H9O)2OPC4H8OPO(C4H9O)2
(C4H9O)2OPOC8H16OPO(C4H9O)2
(C4H9O)3PO
CnH2n+2
C2nH4n+2
Cn-mH2n+2-2m
(CnH2n+1C4H8O)(C4H9O)2PO
HNO3
H2O
O2
Cn-1H2nCO
CnH2n+1NO2
CnH2n+1ONO2
CnH2n+1OH
RCOOH
(HOC4H8O)(C4H9O)2PO
(O2NC4H8O)(C4H9O)2PO
(O2NOC4H8O)(C4H9O)2PO
(C4H9C4H8O)(C4H9O)2PO
(HOOCCnH2nO)(C4H9O)2PO
(CnH2n+1C4H8O)(C4H9O)OPOH
1
1'
1"
2
2'
2"
3
4
5
5'
6
6'
+

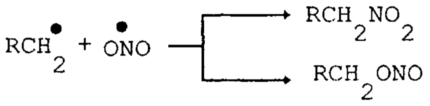
Mailen's Hypothesis

In recent years, only a few research groups have focused their interest on chemical diluent degradation. Using a very extensive and conclusive literature survey as a base, Mailen et al. (63) performed a series of experiments which allowed them to develop a set of reactions for the chemical degradation of normal paraffin hydrocarbon (NPH) diluent. Their findings highlighted several features. First, nitric acid does not produce an independent chemical effect on the nitration of paraffins but serves purely as a source for the formation and regeneration of nitrogen oxides. Second, the radical-like molecule of monomeric nitrogen dioxide (NO_2) is the primary active chemical agent in this reaction. Finally, the initial elementary chemical process in the nitration of a paraffin chain is the formation of organic radicals by interaction with the monomeric NO_2.

The normal paraffin hydrocarbons first react with radical like $^{\bullet}NO_2$ molecules to form a free hydrocarbon radical:

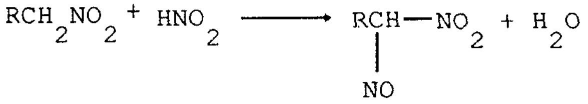
$$RCH_3 + \overset{\bullet}{N}O_2 \longrightarrow RCH_2^{\bullet} + HNO_2 \tag{3}$$

The hydrocarbon radicals ($RCH_2^{\bullet}$) then react with molecule of NO_2 to give nitro or nitrite compounds:



$$RCH_2^{\bullet} + \overset{\bullet}{O}NO \longrightarrow \begin{cases} RCH_2NO_2 \\ RCH_2ONO \end{cases} \tag{4}$$

The hydrocarbon derivatives (RCH_2NO_2) then react with nitrous acid (HNO_2) to form nitroso compounds:



$$RCH_2NO_2 + HNO_2 \longrightarrow \underset{\displaystyle NO}{\underset{|}{RCH}}{-}NO_2 + H_2O \tag{5}$$

Also, the nitro compounds can be hydrolyzed to form carboxylic acids (RCOOH). The nitrite (RCH_2—ONO) compounds formed in Reaction (4) may also hydrolyze to a considerable extent to form alcohols:

$$RCH_2ONO + H_2O \rightleftharpoons RCH_2OH + HNO_2 \tag{6}$$

These are, in turn, oxidized to form carboxylic acids:

$$RCH_2OH + 2\,(O) \longrightarrow RCOOH + H_2O \tag{7}$$

Other work by Merkelin and coworkers (64–66) examined the gaseous and liquid radiolysis products of dodecane and decalin used as diluents. Only hydrogen and an olefin ($C_{10}H_{16}$), with G values* of 4.4 and 0.18, respectively, were observed in the radiolysis of decalin. The yield of hydrogen was found to be dose dependent, although the yield of olefin showed a small decrease with increasing dose. The radiolysis products of dodecane were examined by Merkelin and Razvi (65) using gas chromatography. Paraffins up to $C_{24}H_{50}$ were detected, and their yields appeared to increase with absorbed dose. In the presence of nitrous oxide the yields of intermediate products, C_{17}–C_{20}, and low molecular weight species, C_5–C_{11}, showed significant reductions, yet the yield of the dimer of $C_{24}H_{50}$ was unaffected.

Influence of Diluent on TBP Degradation

Many hydrocarbons have been used as the solvent for TBP in radiolytic experiments. Most of these were designed to evaluate the extent of decomposition of TBP in the test solvent as compared with decomposition in a reference solvent. Although the literature gives confusing results, there is strong evidence that the G value for HDBP production increases with increasing stability of the paraffinic diluent.

Marston et al. (36) claimed that HDBP formation is increased by a factor of 2.7 in changing from kerosene diluent containing naphthenes and isoparaffins to a more stable *n*-paraffin mixture. Recent studies (67, 68) showed the yield of HDBP to increase when carbon tetrachloride was used as the diluent.

The effect of various diluents on the TBP degradation products (as measured by Z number†) (69) was also examined over a range of nitric acid concentrations (50). Using thin-layer chromatography, nitration and oxidation products as well as HDBP, H_2DBP, and phosphoric acid were detected. It was proved that the highest yield of degradation products occurred in the TBP–CCl_4–HNO_3 system. As a result, it was suggested that the considerable amounts of hydrochloric acid produced in the former system accelerated the process of degradation, whereas in the TBP/mesitylene system the aromatic nature of the diluent decreased the yield of degradation products. In addition, the effect of diluent on the yield of nitro and carbonyl compounds was also examined, and it was reported

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* The absolute yields of these products, defined as a G value in units of molecules per 100 eV.

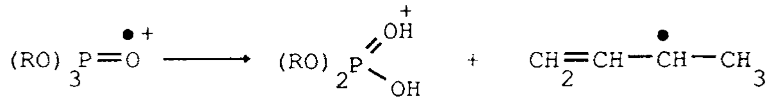
† The Z number is the amount (mol/10^6 L) of zirconium retained by the solvent when it is equilibrated with a mixture of inert and radioactive zirconium of specified concentration and then contacted three times with fresh portions of 3 M HNO_3

that low yields of carbonyl compounds were obtained using mesitylene as a diluent while mesitylene and dodecane diluents both gave low yields of nitro compounds. On the other hand, when carbon tetrachloride was used as a diluent, a high yield of carbonyl compounds but a very low yield of nitro compounds resulted.

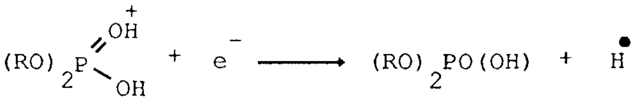
More recent work by Bellido et al. (70) supports earlier results by Canva and Pages (71) on the protective effects of aromatic diluents in reducing the extent of radiolytic degradation of TBP. The enhancement of TBP degradation in the presence of stable diluents can be attributed to the ionization potential of organic substances. This is illustrated by the following set of reactions:

$$[\text{diluent}] \longrightarrow [\text{diluent}]^{\bullet +} + e^{-} \qquad (8)$$

$$[\text{diluent}]^{\bullet +} + (RO)_3P{=}O \longrightarrow (RO)_3P{=}O^{\bullet +} + [\text{diluent}] \qquad (9)$$



$$(RO)_3P{=}O^{\bullet +} \longrightarrow (RO)_2P(\overset{+}{=}OH)(OH) + CH_2{=}CH{-}\overset{\bullet}{C}H{-}CH_3 \qquad (10)$$



$$(RO)_2P(\overset{+}{=}OH)(OH) + e^{-} \longrightarrow (RO)_2PO(OH) + \overset{\bullet}{H} \qquad (11)$$

If the diluent has a higher ionization potential than TBP, Reaction (9) will occur and will result in greater degradation of TBP because of subsequent Reactions (10) and (11). The higher the ionization potential of the diluent, the greater the TBP degradation. The low ionization potential of aromatic compounds (about 9 eV) allows these diluents to act as an "ionization sink," and this protects the TBP molecule against further degradation. The ionization potential of carbon tetrachloride is 11.5 eV while that for an aliphatic diluent often used in reprocessing *n*-dodecane is 10 eV. This behavior of organic substances as diluents suggests the use of aromatic rather than aliphatic compounds to dilute TBP.*

Thermal Degradation of TBP/Diluents

The choice of the TBP as an extractant in nuclear fuel reprocessing because of its chemical inertness has already been noted. Its stability

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* Aromatic diluents have higher densities and lower flash points than aliphatic hydrocarbons.

toward oxidation—in particular its resistance to nitric acid—is excellent (96), although at temperatures above 100°C it may react with nitric acid to form nitro compounds and at even higher temperatures react violently. Acid hydrolysis may occur in either the organic phase or the aqueous phase, and although the rate constants in the organic phase were found to be several orders of magnitude lower than in the aqueous phase, it may be shown that in a two-phase mixture most of the hydrolysis will occur in the organic phase.

The conclusions of early studies by Wagner (73), who investigated the reactions of TBP when mixed with equal volumes of 3 and 6 M nitric acid at elevated temperatures (up to 105°C), were queried by Burger (74) on the basis of certain assumptions made and the kinetic analysis calculational technique employed. Davis and Kibbey (75) subsequently studied the rate of decomposition of TBP in the aqueous phase with 1–5 M nitric acid at temperatures ranging from 35 to 75°C, in which the initial ratio of organic to aqueous phase was about 10^{-4}. However, the rate of HDBP formation was found to be the same as for phase ratios of 10^{-2}. The data appear to indicate that the rate constant for TBP decomposition in the aqueous phase was about an order of magnitude greater than that in the organic phase. During nuclear fuel reprocessing, however, the overall TBP decomposition rate in the organic phase will be some two orders of magnitude higher than in the aqueous phase.

In addition, Nowak et al. (76) examined the thermal degradation of TBP systems. These systems, which consisted of TBP, TBP–dodecane, and TBP–mesitylene, were heated in contact with an aqueous nitric acid phase for 40 hours using an organic/aqueous phase ratio of 2:1. Their findings confirmed HDBP to be present in all systems while organic nitrates only persisted in the first two. Neither carbonyl nor nitro compounds were detected in the system consisting of TBP–dodecane–nitric acid when it was heated to 80°C, in contrast to the result obtained during the radiolysis of this mixture (50); however, in systems heated to 100°C, both carbonyl and nitro compounds were detected. As a result of their research, a mechanism for the formation of carbonyl and nitro compounds was suggested:

$$HNO_3 \rightarrow HO^{\bullet} + NO_2 \qquad (12)$$

$$RCH_3 + HO^{\bullet} \rightarrow RCH_2^{\bullet} + H_2O \qquad (13)$$

$$RCH_2^{\bullet} + NO_2 \rightarrow RCH_2NO_2 \text{ or } RCH_2ONO \qquad (14)$$

$$RCH_2ONO \rightarrow RCHO + HNO \qquad (15)$$

It was suggested that such carbonyl compounds formed would oxidize to carboxylic acids which could be removed by an alkali wash, unlike those carbonyl compounds obtained by radiolysis (77). The decrease in yield of nitrites was observed in systems in which nitro compounds were formed in greater yields. The yield of HDBP and H_2MBP was also influenced by the presence of uranyl nitrate, although only marginally. The general conclusion appeared to be that the yields of most degradation products increased significantly only above 90°C, which is supported by the early research carried out by Dukes (78).

Radiolytic Degradation of TBP/Diluents

Although a wealth of knowledge is available concerning the deleterious effects of radiation on solvent extraction processes for recovering uranium and plutonium from irradiated nuclear fuels, only a small number of publications have been concerned with the radiolysis of undiluted TBP. The phosphate anion, $[PO]_4^{3-}$, in TBP $[(C_4H_9O)_3P{=}O]$ is very stable toward radiation; the rupture of a P—O bond is much less probable than that of a C—O bond, and this was considered to be shown by the low yields of butanol (73). In pure TBP solutions the main liquid degradation product formed is HDBP, and the various reported yields (*G* values) are summarized in Table 1.

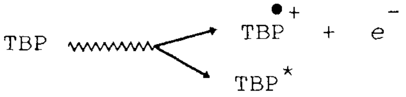
In addition, H_2MBP has been identified as a degradation product, but the yield is approximately 10 times lower than HDBP, varying from 0.12 to 0.39. As the absolute yield of H_2MBP does not increase with increasing concentration of HDBP, Wilkinson et al. (79) concluded that H_2MBP and phosphoric acid are formed from the primary decomposition of the TBP and not from the decomposition of HDBP. Early work by Hardy and Scargill (82) showed that, due to the distribution coefficient between the aqueous and organic phases in the nitric acid–solvent system, any H_2MBP would be extracted into the aqueous phase; consequently, both phases would need to be examined to determine the total acid yield. The replacement of all three butyl groups to give phosphoric acid has only been observed at doses greater than 10^3 Mrads (72).

TABLE 1
G Values for Radiolysis of Tributyl Phosphate

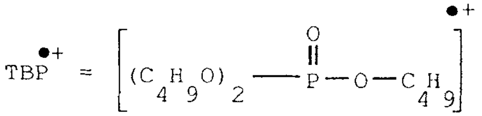
Radiation source	HDBP	H_2DBP	H_2	CH_4	C_2	$C_3 + C_4$	Ref.
1.25 MeV electrons	1.52	0.12	1.11	0.005	0.24	0.45	79
^{60}Co gamma	1.7–1.8	0.3	—	—	—	—	72
1 MeV electrons	2.25	0.39	1.59	0.07	0.13	0.75	80
1.66 MeV electrons	2.44	0.14	1.73	0.07	0.18	0.65	81

Gaseous products, such as saturated hydrocarbons and olefins, are also formed but in amounts much lower than expected on the basis of formation of HDBP and H_2MBP; however, yields of hydrogen have been found to be comparable with those of HDBP as shown in Table 1. Other species, such as high molecular weight polymers, have been detected (35, 76), although estimates of yields vary by a factor of 3; laboratory experiments of radiolysis of TBP in the presence of HNO_3 have also detected hydroxamic acids, carbonyl compounds, nitro compounds, and long-chain monomeric and dimeric phosphate esters. These are all examined in further detail in the following section.

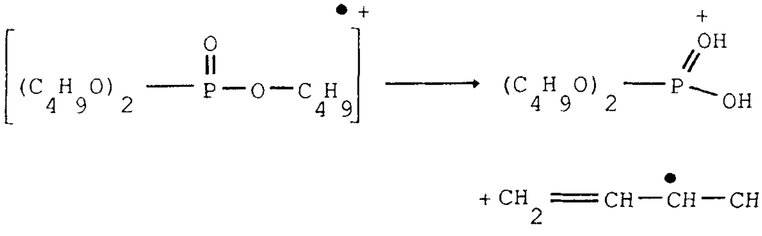
It is evident from the Table 1 that there are discrepancies in the results of various workers. This is attributed to the different dosimetric procedures employed. In early work, Burr (81) suggested a tentative free-radical mechanism from excited molecules for the formation of the various degradation products. Wilkinson et al. suggested mechanisms based on fragmentation followed by rearrangement of the primary ion (M^+) before neutralization. Their findings were based on identification of the species $(RO)_2P(OH)_2^+$ from mass spectra; this ion was considered to be formed by an initial decomposition accompanied by rearrangement, while other species such as $PO{\cdot}P(OH)_3^+$ and $P(OH)_4^+$ resulted from further fragmentation of $(RO)_2P(OH)_2^+$. Reactions such as those indicated below were postulated:



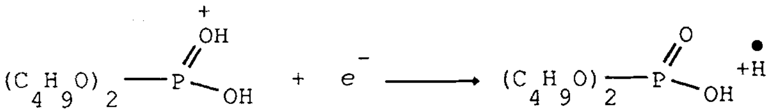
$$\mathrm{TBP} \rightsquigarrow \mathrm{TBP}^{\bullet+} + e^- ;\quad \mathrm{TBP}^{\star} \qquad (16)$$



$$\mathrm{TBP}^{\bullet+} = \left[(C_4H_9O)_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}O{-}C_4H_9\right]^{\bullet+}$$



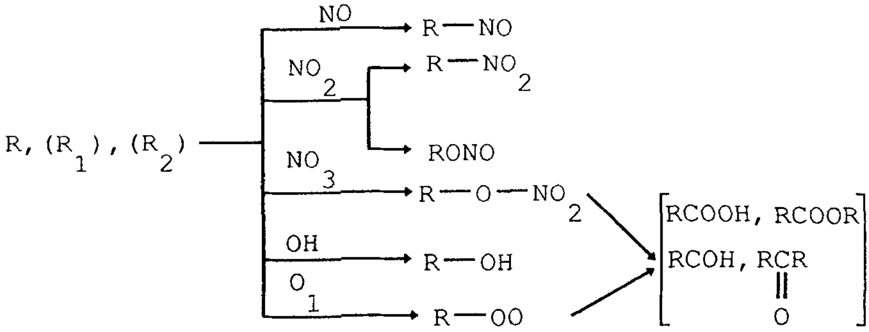
$$\left[(C_4H_9O)_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}O{-}C_4H_9\right]^{\bullet+} \longrightarrow (C_4H_9O)_2{-}P(=\overset{+}{O}H){-}OH + CH_2{=}CH{-}\overset{\bullet}{C}H{-}CH_3 \qquad (17)$$


(18)

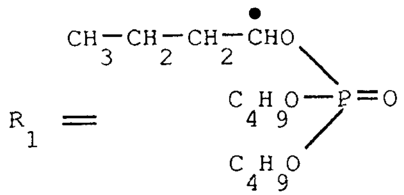
The rearrangement in Reaction (17) occurred with the loss of a hydrocarbon fragment as a radical and was consistent in that hydrocarbon ions were not abundant in the mass spectrum. Resonance of the positive charge between the attached hydroxyl groups may give such ions extra stability. In addition, the small yields of H_2DBP were also assumed to arise from primary decomposition of TBP and not secondary decomposition of HDBP, since the yield of H_2DBP did not increase as the concentration of HDBP increased in the irradiated mixture.

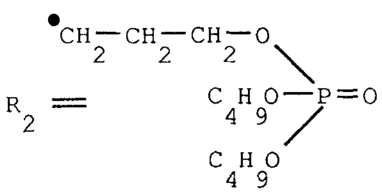
Nowak and coworkers (50, 76, 83–95) investigated extensively the degradation of irradiated TBP/nitric acid/hydrocarbon systems. Early results (76, 84) reported the detection of stable radicals during an electron spin resonance study (ESR) of the system, with the maximum concentration of radicals in 1 M nitric acid irradiated systems. Lower concentrations of these radicals were observed in undiluted systems. However, their presence was not noted when the system was irradiated in the absence of nitric acid. The second publication included the effects of ultraviolet light and thermal degradation. Furthermore, at low nitric acid concentration (< 2 M nitric acid) using gamma irradiation, more than half of the potential zirconium complexing compounds remained in the solvent after alkaline wash, whereas in the case of ultraviolet or thermally degraded solvent systems most of the zirconium complexing compounds were removed by alkaline wash over the whole range of nitric acid concentrations investigated. In all three degradation techniques, gamma irradiation, thermal degradation, and ultraviolet treatment, the major degradation species were assumed to be HDBP and H_2DBP.

Nowak (50) considered the extent to which changes in dose rate, energy, and nature of the radiation as well as exposure time affected the yield of final products and properties of TBP. The formation of nitro and carbonyl compounds was examined in the TBP–nitric acid–water system, when the amount of nitro compounds produced was found to increase with nitric acid concentration whereas the yield of carbonyl compounds showed a maximum at 3 M nitric acid, and only above 7 M nitric acid did the yield of nitro compounds predominate over carbonyl compounds. No correlation could be made between Z number and nitro and/or carbonyl concentration in relation to nitric acid concentration. At low (< 1 M) nitric acid concentrations, formation of hydroxamic acids was observed, but not at higher acidities because of its oxidation by nitrous acid. This is illustrated in the following scheme:



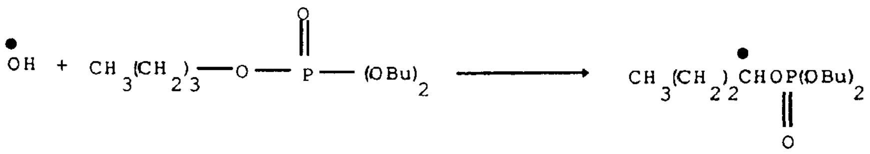
where R = alkyl radical





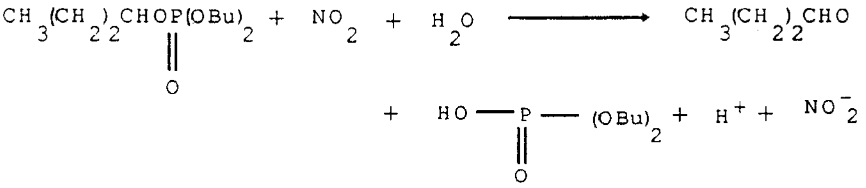
Work by Healy and Pilbeam (48) resulted in the suggestion that metal retention in irradiated solvent could be caused by the presence of hydroxamic acids, which was in disagreement with earlier work by Stieglitz, who had proposed that carbonyl compounds were responsible for this effect. There is now good evidence that the principal metal retention ligands in irradiated solvents are long-chain alkyl-phosphoric acids and possibly to a lesser extent polycarbonyl compounds.

Clay and Witort (97) examined the radiolysis of TBP in aqueous solution, and once more confirmed the major degradation product to be HDBP. Although a number of carbonyl compounds were qualitatively detected, only butyraldehyde was positively identified. These carbonyl compounds were not detected when the solutions were made up to 4 M in HNO_3, indicating their susceptibility to postradiolytic attack in the presence of nitric acid at higher concentrations. In addition, the *G* values for HDBP decreased as nitric acid concentration increased. It was therefore proposed that the chemical attack of the TBP was caused by the production of hydroxyl radicals by radiolysis in the aqueous solution:



$$^{\bullet}OH + CH_3(CH_2)_3{-}O{-}P(=O){-}(OBu)_2 \longrightarrow CH_3(CH_2)_2\overset{\bullet}{C}HOP(=O)(OBu)_2$$

Their postulated reaction scheme, suggesting that in oxygenated solutions these reactions could proceed by the addition of oxygen to the radical site which results ultimately in the decomposition of TBP to produce HDBP and other products arising from the butyl chain, such as butyraldehyde, is purely speculative. In the absence of oxygen the radicals must react by alternative routes, producing a lower yield of HDBP. In the absence of nitric acid, however, no such effect of oxygen was noted, the yields of HDBP being similar in both oxygenated and deoxygenated solutions. This observation could be associated with the reactions of NO_2 produced by the radiolysis of nitric acid, for example:



$$CH_3(CH_2)_2CHOP(=O)(OBu)_2 + NO_2 + H_2O \longrightarrow CH_3(CH_2)_2CHO + HO{-}P(=O){-}(OBu)_2 + H^+ + NO_2^-$$

The decrease in the yield of HDBP observed at high HNO_3 concentrations was attributed to reaction of OH radicals with undissociated nitric acid in competition with the $OH^{\bullet}$ radical attack of the TBP:

$$\overset{\bullet}{O}H + HNO_3 \longrightarrow H_2O + \overset{\bullet}{N}O_3$$

It was also observed that in neutral and dilute acid solution the *G* value for HDBP was slightly less than the G-value for $OH^{\bullet}$, indicating that HDBP was not the only product derived from $OH^{\bullet}$ radical attack on TBP; this was supported from evidence of the presence of carbonyl compounds containing the phosphate group (97).

Experiments by Becker et al. (58, 59) attempted to isolate the complexing agents responsible for the reduced efficiency of the solvent extraction system. After irradiation of a 20% TBP/dodecane mixture in contact with nitric acid, the acid degradation products were removed by alkali washing and the lighter volatile residues were isolated by distillation with any remaining complexing species in the residue separated by liquid chromatography. It proved impossible, however, to achieve isolation of the individual components by this chromatographic technique although separation into three groups was achieved. Gas chromatographic and mass spectroscopic analyses enabled the identification of nonpolar species (45%) and neutral phosphate esters (35%).

Nowak et al. (76) reported the influence of dose rate, temperature, nitric acid concentration, and metallic ions (uranium, molybdenum, palladium, and zirconium) on the radiolytic degradation of systems consisting of TBP/dodecane/nitric acid. Their observations indicated that the yields of HDBP and H_2DBP were only slightly influenced by dose rate, temperature, and nitric acid concentrations, but that the presence of uranyl ions markedly increased the yields of these two acidic phosphate degradation products. In contrast, an increase in nitric acid concentration from 0.5 to 3.0 M resulted in an increase in nitro and carbonyl compounds concentration. The yield of organic nitrates showed a similar increase to those previously found for nitro and carbonyl compounds (50), and it was augmented by the presence of uranyl nitrate.

There have been several subsequent independent attempts to identify which particular degradation products are ultimately responsible for the retention of heavy metals. Yongin et al. (25) investigated all the potential degradation species over a series of tests in which they concluded that although the known species, including HDBP, H_2DBP, and long-chain phosphoric acids, did form strong complexes with metal ions, they were not solely responsible and in fact some other unidentifiable radiolytic products with much stronger complexing abilities must be involved.

Experiments involving irradiating a solvent mixture consisting of 30% TBP/OK/H_2O but free from nitric acid also showed metal retention. It was concluded, therefore, that nitro compounds cannot be the precursors for the formation of these strong complexants, and instead they are formed from the combination of H_2DBP and alkyl radicals, identified by ESR studies (98).

In more recent work (99), the extraction behavior of ^{95}Zr with TBP–OK irradiated by various gamma doses (10^2–10^6 Gy) was investigated. It was found that the distribution coefficient of ^{95}Zr increases sharply with an increase in dose rates and nitric acid concentrations. At doses of $> 2 \times 10^6$ Gy and nitric acid concentration ≥ 3 M, the relative ^{95}Zr retention is $\geq 95\%$, while for doses $> 10^5$ Gy, the washing (5% $NaCO_3$) of the organic phase containing ^{95}Zr was more difficult to achieve, with an emulsion being formed. The authors also investigated several known species in turn, including hydroxamic acids, monoalkylphosphate, nitrobenzene, and 1-nitrobutane, to observe the effects on overall metal retention and to allow comparison to their previous findings. They obtained the greatest metal retention with hydroxamic acid and monoalkylphosphate. In addition, they found that removal by alkali washing (5% $NaCO_3$) of hydroxamic acid was more difficult to achieve than that of monoalkylphosphate H_2DBP. However, in the latter case an emulsion was formed.

Theoretical Studies

The main primary degradation products present in the solvent are organic nitrates, nitroalkanes, nitrites, and nitronic acids, along with several compounds such as oximes, ketonitroalkanes, and nitroolefins. Among these compounds, nitro compounds (100) have proven to be valuable intermediates, and the chemical literature continuously reports progress in their utilization for the synthesis of a variety of target molecules. They can be considered as versatile building blocks and intermediates in organic chemistry. In fact, it is possible to have a wide range of efficient methods for their transformation into other significant compounds.

The conversion of the nitro group into a carbonyl group can be considered by far the most important one because it effectively reverses the polarity of the neighboring carbon from nucleophilic to electrophilic, thus allowing a wide range of transformations to be carried out. The reaction was discovered in 1894 by Nef (101) and is currently called the Nef reaction. The mechanism of the Nef reaction has been studied extensively (101–104). The initial conversion of the nitro compound into the salt "nitronate" is accomplished with base; however, the key step is acidification of this intermediate to give the carbonyl compound. This is pH-dependent, and side reactions can occur (see Table 2) (51). Weakly acidic conditions favor regeneration of the nitro compound, whereas high acidity gives the Nef reaction (105). Oximes and pseudonitroles (α-nitroso nitro compounds) are observed at intermediate levels of acidity (pH 1–5).

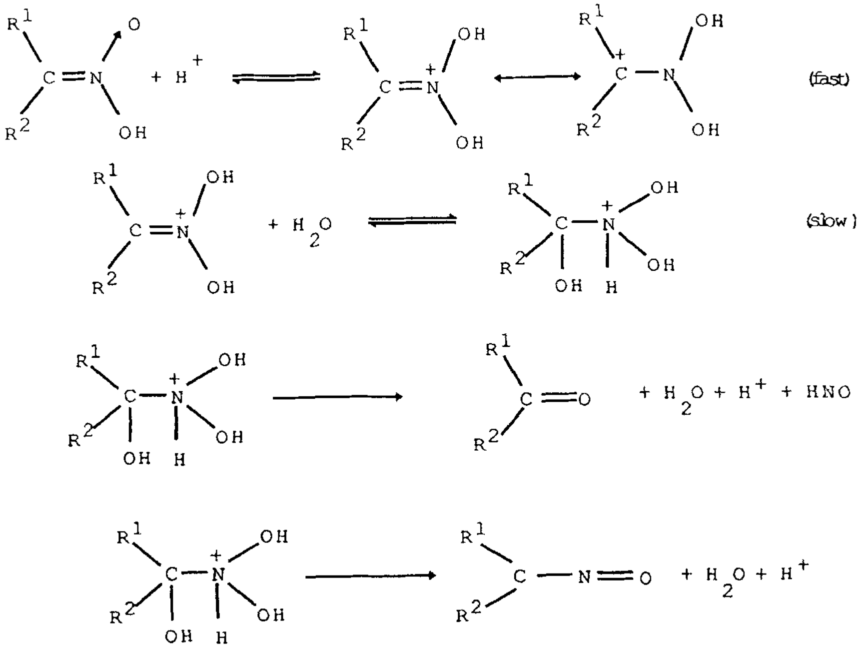
TABLE 2
pH Dependence of the Product Distribution in the Acidification of the Salt of 2-Nitropropane at 21°C

pH	$(CH_3)_2CHNO_2$	$(CH_3)_2C{=}O$	$(CH_3)_2C{=}NOH$	$CH_3C(NO)NO_2$
5.4	100	0	0	0
5.0	85	8	8	0
4.3	44	20	19	15
3.1	10	30	30	29
2.0	0	39	32	29
1.5	0	49	28	22
1.2	0	80	12	7
0.5	0	100	0	0

Several mechanisms have been proposed for this reaction (102, 103, 106). Kinetic analysis, together with the fact that additional water slows the reaction (106), have led to the conclusion that two mechanisms can operate—the difference between the two mechanisms being the timing of water loss. The basic steps are sequential protonation of the nitronate salt on each oxygen followed by attack of water and decomposition of the resulting intermediate. It is clear that the reaction is sensitive to both pH and concentration of water.

The extent to which nitronic acids tautomerize to nitroalkanes instead of undergoing Nef reaction is strongly dependent on the acidity of the medium and the stability of the nitronic acid. In excess of dilute mineral acid, salts of primary nitroalkanes give an aldehyde, and salts of secondary nitroparaffins give ketones. However, when primary nitroparaffins are treated with hot, concentrated acid, the corresponding carboxylic acids and hydroxylamine are produced (43, 110–112). This process involves hydroxamic acids as intermediates, and is known as the Meyer reaction.

The mechanism of the Meyer reaction has been investigated extensively (103, 107–109). A thorough study of the kinetics indicated that the reaction proceeds at a maximum rate at a pH less than that required to protonate all of the neutral nitronic acid (107, 108). This suggests that a competitive reaction takes place involving *O*-protonation of the nitronic acid, followed by loss of water and a proton to give the nitrile oxide (109).



Although the theory states that temperatures below 5°C are required to minimize Nef and other decompositions (113), technological constraints make the use of low temperatures impractical in the process. Therefore the Nef reaction would be predominant and will take place in the process.

Speculation about the mechanisms of degradation, which might be said to have started with Lane's hypothesis (41), is thus far from complete, nor is it ever likely to be. There are surprises to come.

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