Determination of the Degradation Compounds Formed by the Oxidation of Thiophosphinic Acids and Phosphine Sulfides with Nitric Acid

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The degradation process that takes place at room temperature when bis(2,4,4-trimethylpentyl)monothiophosphinic acid ($R_2P(S)OH$), bis(2,4,4-trimethylpentyl)dithiophosphinic acid ($R_2P(S)SH$) and tris(2,4,4-trimethylpentyl)phosphine sulfide (R_3PS) are in contact with 5 M HNO_3 has been studied by FT-Infrared, FT-Raman spectroscopy and by gas chromatography with mass spectrometry detection (GC-MS). An exposure period of ten days of the rough reagents to 5 M HNO_3 causes complete oxidation of the compounds. This process mainly leads to the formation of nitrogen dioxide, elemental sulfur and the oxo-analogues of the reagents. For dilute solutions of the reagents it was observed that after 15 min of contact with phase-shaking, $R_2P(S)OH$ and R_3PS are completely oxidized to yield $R_2P(O)OH$ and R_3PO , respectively, whereas for $R_2P(S)SH$, the oxidation process is less severe, because the dithioacid is still present in the oxidized mixture, the oxidation products being $R_2P(S)OH$ and $R_2P(O)OH$.

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Introduction

In recent years, considerable work has been focussed on the study of metal ion extraction from different aqueous media by commercial extractants based on the thiono-derivatives, bis(2,4,4-trimethylpentyl)thiophosphinic and bis(2,4,4-trimethylpentyl)dithiophosphinic acid.

One of the problems with earlier generations of sulfur-containing extractants was their poor hydrolytic stability and also their tendency to be oxidized by strong oxidizing agents. In this sense, these thiophosphinic acids are known to be more stable towards hydrolysis.¹⁻⁴ However, it has been reported that contact with nitric acid concentrations greater than 2 M causes degradation of the reagents.⁴

This oxidation process complicates the study of the extraction of metal ions from nitric acid media because, on the one hand, there is a less amount of the starting reagent available and, on the other, the metal ions can be extracted by the oxidized species rather than by the species of interest. For all of these reasons, it is necessary to know the rate of decomposition of the reagents in the presence of nitric acid as well as to identify the decomposition compounds.

The deactivation process that these thiophosphinic acids suffer on contact with 5 M HNO_3 has been studied previously by applying FT-Raman spectroscopy.⁵ This technique allowed researchers to confirm the cleavage of the sulfur containing bonds, and also suggested that the degradation processes of these compounds could also give rise to the formation of their oxo-analogues.

However, one of the drawbacks of FT-Raman spectroscopy is that it is not a useful technique for confirming the presence of

functional groups containing oxygen.

Concerning the oxidation products, the formation of disulfides has been reported on the oxidation of dipropyl, diphenyl and bis(2,4,4-trimethylpentyl)dithiophosphinic acids with $Au(III)$, $Cu(II)$ and concentrated nitric acid.^{4,6,7} Furthermore, phosphine oxide and diphenylphosphinic acid have been postulated to be formed by the oxidation of phosphine sulfides and diphenylthiophosphinic derivatives, respectively, with concentrated nitric acid.^{8,9}

Therefore, in an attempt to provide additional information on the degradation process of these phosphorus compounds containing the thiono group $P=S$ by nitric acid we undertook this study.

The stability of these $P=S$ compounds has been studied by using the extractants Cyanex 302[®] and Cyanex 301[®] whose major components are bis(2,4,4-trimethylpentyl)monothiophosphinic acid ($R_2P(S)OH$) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid ($R_2P(S)SH$), respectively. Cyanex 301[®] also has a large amount of tris(2,4,4-trimethylpentyl)phosphine sulfide (R_3PS).^{1,2}

In the present study, FT-IR and GC-MS techniques were applied, because the IR spectroscopic study gives a better understanding of the degradation process and GC-MS allows an exact determination of the decomposition products formed by the oxidation of these compounds with 5 M HNO_3 . To our knowledge, no previous GC-MS study of the degradation compounds has been undertaken.

The degradation of the rough reagents was studied by analyzing the organic phases by FT-IR spectroscopy. Moreover, the identification of the degradation compounds was based on the GC-MS analysis of dilute solutions of the extractants in toluene.

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Experimental

Reagents

Cyanex 302®, Cyanex 301® and Cyanex 272® were kindly supplied by Cytec Canada Inc. and used as delivered. Toluene (Merck, p.a.) was used as a diluent. *N,N*-Dimethylformamide dimethylacetal (Aldrich, 94%) was used as the derivatization reagent. Celite 545 (Merck) was used to filter the extractants. Aqueous solutions were prepared from HNO₃ (Merck, p.a.).

Instrumentation

Infrared spectra were recorded using a Mattson 1000 FT-IR. The samples were measured as a liquid within two KBr plates.

Raman spectra were recorded using a Nicolet 950 FT-RAMAN Spectrometer equipped with an InGaAs detector. Excitation at 1064 nm was provided by an Nd:YAG laser operating at 1000 mW. Data were collected at a spectral resolution of 8 cm⁻¹ and 100 scans were accumulated.

GC-MS analysis was performed on an HP Series 5890A gas chromatograph (Hewlett-Packard) coupled to an HP5989B mass selective detector. The data were processed using an HPG1034C MS Chem. Station.

The chromatographic separations were carried out using a fused-silica capillary column (12.5 m × 0.25 mm × 0.25 μm) filled with crosslinked 5% phenylmethyl silicone (HP-5). Helium was used as a carrier gas at a pressure of 69 kPa. The oven was programmed to heat the column from 50 to 300°C at a rate of 10°C min⁻¹, and then held at 300°C for 10 min. The injector temperature was 290°C and the detector temperature was 300°C. A 0.2 μl sample of the solution was injected manually into the column in the splitless mode.

Detection of the different compounds was performed in the scan mode in the mass range between *m/z* 50 and 650. The ion source temperature was 200°C and the quadrupole temperature was 100°C. The ionizing energy was 70 eV.

Similar chromatographic conditions had been used previously for the separation of components and their determination in Cyanex 302® and Cyanex 301® reagents.^{10,11}

Infrared and Raman spectroscopy analysis

To more easily identify the decomposition compounds, the extractants were used without a diluent. Equal volumes of the rough extractants and 5 M HNO₃ were contacted and shaken at room temperature for 15 min. After that the extractants were kept in contact with the aqueous phase, 10 days later the organic phases were removed, filtered through free crystalline silicic acid (Celite 545) and analyzed by FT-Infrared spectroscopy. Previous experiments confirmed that this period of time was sufficient to achieve complete oxidation of the starting material. The yellow solid that appeared at the interface was separated, filtered, washed several times with ether, dried under a vacuum and analyzed by FT-Raman spectroscopy.

GC-MS analysis

This study was performed with a dilute solution of the extractants. The aqueous phases contained 5 M HNO₃, while the organic phases contained 2.5 g l⁻¹ of either Cyanex 302® or Cyanex 301® in toluene. Equal volumes of each extractant solution and 5 M HNO₃ were contacted and shaken at room temperature for 15 min. After phase separation using a high-speed centrifuge (Centaur 2 MSE), the organic layers were removed, washed several times with distilled water and finally filtered through free crystalline silicic acid (Celite 545). Then, 1 ml of the organic phases was reacted with an excess of *N,N*-

Fig. 1 (a) Raman spectrum of the yellow solid originated after the contact of rough Cyanex 302® with 5 M HNO₃. Infrared spectra of (b) Cyanex 302®, (c) Cyanex 302® after contact with 5 M HNO₃ and (d) Cyanex 272®.

dimethylformamide dimethylacetal for 1 h at 65°C.^{1,12} After the solution resulting from the reaction was allowed to cool, a GC-MS analysis was carried out immediately.

Results and Discussion

Cyanex 302® (Infrared and Raman spectroscopy)

The first signs that indicated that the degradation process had started were the formation of a yellow solid at the interface and the evolution of a brown gas (NO₂) through the organic phase.

The Raman spectrum of the yellow solid obtained after the extractant had been in contact with 5 M HNO₃ for ten days is shown in Fig. 1a. It is undoubtedly the spectrum of sulfur. This diagnosis was confirmed by a comparison of this spectrum with that of a sample of elemental sulfur.

The infrared spectra of the rough extractant before and after contact with 5 M HNO₃ for 10 days are collected in Figs. 1b and c, respectively, whereas Fig. 1d illustrates the infrared spectrum of Cyanex 272®, which was recorded for purpose of a comparison.

The sample of rough Cyanex 302®, used as received, contained approximately 85% of R₂P(S)OH. The extractant also contained about 12% of R₃PO and small quantities of R₂P(O)OH, R₂HPO and R₂P(S)SH. Taking into account that Cyanex 302® was used without any further purification, the presence of minor compounds complicates the spectra. However, because they are present at very negligible amounts, except for tris(2,4,4-trimethylpentyl)phosphine oxide (R₃PO), their presence probably does not affect any of the relevant conclusions.

The spectrum of the extractant before any contact (Fig. 1b) shows in the high-frequency region broad intense absorption bands characteristic of an organophosphorus acid. The presence of only two absorption bands and their frequencies of about 3000 and 2330 cm⁻¹, indicates that the acid is a P(S)OH compound. The spectrum also shows the two absorption

characteristics of the P=S group, the doublet at 738 and 724 cm^{-1} (P=S(I)) and the doublet at 607 and 597 cm^{-1} (P=S(II)).¹³ According to Nyquist,¹⁴ these bands occur as a doublet due to the existence of rotational isomers. The strong absorption band at 918 cm^{-1} corresponds to the P-O stretching vibration in the P-O-(H) bond. The absence of the S-H stretch in the 2600 – 2550 cm^{-1} region rules out a thiol structure. The medium band at 819 cm^{-1} corresponds to the P-C stretching vibration. The C-H stretching frequencies occur at 2953, 2906 and 2869 cm^{-1} . The C-H deformation vibrations have frequencies of 1477 and 1469 cm^{-1} and multiple bands in the 1365 – 1395 cm^{-1} region confirm the presence of more than one CH_3 group on a carbon atom. The absorption bands at 1238 and 1199 cm^{-1} are assigned to the C-C stretch of the tert-butyl group.¹⁵

Finally, the presence of R_3PO , R_2HPO and $\text{R}_2\text{P(O)OH}$ in the extractant is evidenced by the appearance of two medium bands at 1161 and 1117 cm^{-1} that must arise from the P=O stretching vibration of these compounds. However, the phosphoryl vibration of compounds of the type R_3PO , which is the most abundant, is expected to appear in the range 1150 – 1183 cm^{-1} .¹³ The band at 1117 cm^{-1} is outside this range. The lowering of the phosphoryl frequency can be attributed to hydrogen bonding between the phosphoryl oxygen of the R_3PO compound and the hydrogen in the OH group of the monothiophosphinic and the phosphinic acids.

Figure 1c shows that many spectral changes occur upon contact of the thiophosphinic acid with 5 M HNO_3 . These changes involve a disappearance of the bands corresponding to the presence of sulfur in the reagent and the developing of new absorption bands. Thus, the bands in the region 738 – 597 cm^{-1} corresponding to the P=S group have disappeared, and the two characteristic absorption bands of a P(S)OH acid in the high-frequency region have been replaced by three bands at approximately 2670, 2330 and 1642 cm^{-1} , which suggest that a P(O)OH compound has been formed. The fact that the 1642 cm^{-1} band is by far the strongest of the three indicates that the compound is a phosphinic acid.¹³ This assumption is confirmed by the presence of a strong band at 1171 cm^{-1} corresponding to the P=O stretch.¹⁶⁻¹⁸ The band corresponding to the P-O(H) vibration shifts and appears at 959 cm^{-1} . The stretching and deformation vibrations of the 2,4,4-trimethylpentyl group appear at nearly the same frequency as that observed for the sample of Cyanex 302®.

The infrared spectrum suggests that $\text{R}_2\text{P(S)OH}$, the major component of Cyanex 302®, has been oxidized to its phosphinic analogue. In order to confirm this assumption the infrared spectrum of a sample of Cyanex 272®, that contained approximately 84% of $\text{R}_2\text{P(O)OH}$ and 14% of R_3PO , was recorded and is shown in Fig. 1d.

The spectrum shows that the commercial reagent contains an organophosphorus acid, as indicated by the three broad absorption bands at about 2685, 2314 and 1675 cm^{-1} that can be attributed to a P(O)OH group. The relative intensities of these absorption bands together with the frequency (1172 cm^{-1}) corresponding to the phosphoryl stretching vibration confirm that the acid is a phosphinic acid. The strong absorption band at 959 cm^{-1} corresponds to the P-O stretching vibration in the P-O-(H) group. The medium band at 819 cm^{-1} corresponds to the P-C stretching vibration.

The reagent also contains tris(2,4,4-trimethylpentyl)phosphine oxide (R_3PO), which has a characteristic band in the region 1150 – 1183 cm^{-1} corresponding to the phosphoryl stretching vibration. In this sense, the width and intensity of the band centered at 1172 cm^{-1} suggest that it results from the superposition of the bands due to the P=O stretching vibration of

Fig. 2 Gas chromatograms of Cyanex 302® in toluene (a) before and (b) after contact with 5 M HNO_3 . (R = 2,4,4-trimethylpentyl). Peaks: 1 = $\text{R}_2\text{PO}_2\text{CH}_3$; 2 = R_2HPO ; 3, 4, 5 = isomers of R_2PSOCH_3 ; 6 = R_2PSOCH_3 ; 7 = $\text{R}_2\text{PS}_2\text{CH}_3$.

both compounds.

A comparison of Figs. 1c and d shows that the spectrum of the sample of Cyanex 302® after being in contact with 5 M HNO_3 looks like that of Cyanex 272®, but is not identical. Figure 1c shows an absorption band at 3450 cm^{-1} which indicates that the sample is wet. The presence of a small amount of water could account for the shape of the band at 1642 cm^{-1} . On the other hand, the band at 819 cm^{-1} due to the P-C stretching vibration presents a lower intensity than in the spectrum of Cyanex 272®, meaning that some damage to the alkyl chains has taken place.

Cyanex 302®(GC-MS)

Figure 2 shows the gas chromatograms of the organic extractant in toluene before and after contact with 5 M HNO_3 . The identity of the compounds present in Cyanex 302® has been reported previously.¹⁰ The main identified compounds are included in the figures whereas the minor ones are listed in the caption of Fig. 2. A comparison of the two gas chromatograms shows that the monothio compound and also two minor components have been eliminated, whereas the peak at the retention time corresponding to the phosphinic acid derivative increases and another peak at a retention time of 19.60 min has been formed.

The mass spectrum of the intense peak at a retention time of 11.22 min is collected in Fig. 3. The mass spectrum shown provides much more structural information than the IR spectrum and structural confirmation could be made by comparing the molecular and fragment ions with the known fragmentation pathway of the methyl ester of $\text{R}_2\text{P(O)OH}$. The fragmentation process of this compound is discussed in a previous paper.¹¹ This compound gives a low $M + 1$ peak at $m/z = 305$. The base peak at $m/z = 108$ that can be assigned to the ion $[(\text{CH}_3)(\text{CH}_2)\text{PO}(\text{CH}_3)\text{OH}]^+$ could be originated by two consecutive McLafferty rearrangements. Other characteristic ions are: $[\text{C}_4\text{H}_9]^+$ ($m/z = 57$), $[\text{M}-\text{CH}_3]^+$ ($m/z = 289$), $[\text{M}-\text{C}_4\text{H}_9]^+$ ($m/z = 247$), $[\text{M}-\text{C}_5\text{H}_{11}]^+$ ($m/z = 233$) and $[\text{M}-\text{C}_8\text{H}_{17}]^+$ ($m/z =$

Fig. 3 Mass spectrum of the methyl ester of bis(2,4,4-trimethylpentyl)phosphinic acid (compound 1 in Fig. 2).

191).

The GC-MS analysis also confirms that $R_2P(S)OH$ has been oxidized to $R_2P(O)OH$. Compound 9 was not, however, identified.

Cyanex 301® (Infrared and Raman spectroscopy)

Similarly to Cyanex 302®, Cyanex 301®, that has initially been shaken for 15 min and then left in contact with an aqueous solution of 5 M HNO_3 , undergoes decomposition over a period of days at room temperature, as is evidenced by the formation of a yellow solid at the interface and the evolution of a brown gas (NO_2) through the organic phase.

The sample has been used without further purification, and contains about 77.2% of $R_2P(S)SH$. The other components being, R_3PS , $R_2P(S)OH$ and $R_2P(O)OH$.¹¹ The most characteristic IR vibrational bands of the rough extractant should be due to its major component, $R_2P(S)SH$.

Figure 4a shows the Raman spectrum of the yellow solid which was originated by the process, and confirms that the sulfur present in the reagent was eliminated.

The infrared spectra of the rough extractant before and after contact with 5 M HNO_3 for 10 days are collected in Figs. 4b and c, respectively, whereas Fig. 4d illustrates the infrared spectrum of Cyanex 272®.

Dilute solutions of phosphinodithioic acids show a sharp band at about 2560 cm^{-1} corresponding to the S-H stretch. However, when these compounds are undiluted, the band due to this vibration shifts and appears as a broad band at about 2420 cm^{-1} . In this sense, the spectrum shows a broad band at about 2397 cm^{-1} and also a sharp, small band at 2578 cm^{-1} that can be assigned to the S-H stretching vibration. Taking into account that the band at 2397 cm^{-1} disappears in dilute solutions, it must arise from the S-H stretch which is intermolecularly hydrogen bonded. According to Allen and Colclough,¹⁹ the complexity of the broad band at 2397 cm^{-1} may be due to the presence of a mixture of hydrogen-bonded polymers of the type $(R_2P(S)SH)_n$.

Two other vibrations are expected for the S-H group. The one due to a displacement of hydrogen in the S-P-S plane and that corresponding to a displacement of hydrogen perpendicular to the S-P-S plane. According to Nyquist¹⁴ the former should appear at about 800 cm^{-1} and the latter at a frequency below 400 cm^{-1} .

The bands characteristic of a P=S group also should be observed as the reagent contains mainly a dithiophosphinic acid, as well as a considerable amount of a phosphine sulfide (~16%) and a small quantity of a monothiophosphinic acid. The presence of a P=S bond in $R_2P(S)SH$ should result in two absorption bands with frequencies within the ranges 731 cm^{-1}

Fig. 4 (a) Raman spectrum of the yellow solid originated after contact of rough Cyanex 301® with 5 M HNO_3 . Infrared spectra of (b) Cyanex 301®, (c) Cyanex 301® after contact with 5 M HNO_3 and (d) Cyanex 272®.

(P=S(I)) and $595 - 617\text{ cm}^{-1}$ (P=S(II)), whereas R_3PS the second most abundant in the mixture, should exhibit two absorption bands within the frequency regions $685 - 800\text{ cm}^{-1}$ (P=S(I)) and $535 - 599\text{ cm}^{-1}$ (P=S(II)).¹³

In this spectrum a strong band is recorded at 611 cm^{-1} (P=S(II)) that arises from the P=S stretching vibration of $R_2P(S)SH$, R_3PS and $R_2P(S)OH$. However, the spectrum shows that the frequency region corresponding to the P=S(I) band is very complex. There are three main absorption bands with frequencies of 712 , 733 and 805 cm^{-1} . The absorption band at 805 cm^{-1} is very broad and complex and several weak bands can be detected superimposed on its profile. By comparison with the spectrum of the samples of Cyanex 272® and Cyanex 302® other modes such as P-C stretching vibration have been assigned in this region. On the other hand, as mentioned above, the vibration due to the displacement of hydrogen in the S-P-S plane should occur in this region. For all of these reasons it is very difficult to assign these bands with certainty.

Two bands are observed at 489 and 454 cm^{-1} that can be assigned to the P-S stretching vibration of $R_2P(S)SH$.

The presence in the sample of $R_2P(O)OH$ is evidenced by the appearance of a weak band at 1161 cm^{-1} corresponding to the P=O stretching vibration of this compound.

The spectrum of the sample after contact with 5 M HNO_3 for ten days is illustrated in Fig. 4c. It is noticeable that the broad band centered at 2397 cm^{-1} corresponding to the S-H stretching vibration has disappeared and three new bands at about 2670 , 2330 and 1645 cm^{-1} , that are usually associated with the P(O)OH group of an organophosphorus acid, have been originated. On the other hand, the bands in the region $805 - 454\text{ cm}^{-1}$ corresponding to the presence of P(S)SH and P-S groups in the sample have disappeared and new bands at 1172 and 959 cm^{-1} , which undoubtable arise from the P=O stretch and the P-O(H) vibration respectively, have been formed. The frequencies of the infrared absorption bands observed for these oxidized sample are similar to those observed for the sample of Cyanex 302® after a nitric acid treatment and for Cyanex 272®,

Fig. 5 Gas chromatograms of Cyanex 301® in toluene (a) before and (b) after contact with 5 M HNO₃ (R = 2,4,4-trimethylpentyl).

which seems to indicate that both thiophosphinic acids and the phosphine sulfide have been oxidized to the phosphinic acid and phosphine oxide analogues, respectively.

Cyanex 301® (GC-MS)

Figure 5 shows the gas chromatograms of the organic extractant in toluene before and after contact with 5 M HNO₃. The reagent composition has been described previously.¹¹ It can be observed that the phosphine sulfide has disappeared and the concentration of the dithio compound has decreased, whereas the monothio compound is still present in the sample after contact with nitric acid. The peak at the retention time of the phosphinic acid derivative increases significantly and several new compounds have been originated, the most intense being the one at a retention time of 14.99 min.

The mass spectrum of the intense peak at a retention time of 11.19 min, which is collected in Fig. 6a, shows the same fragmentation pattern as that observed in Fig. 3, which confirms that the compound is the methyl ester of bis(2,4,4-trimethylpentyl)phosphinic acid.

The mass spectrum corresponding to the compound at a retention time of 14.99 min is collected in Fig. 6b. This compound shows the same fragmentation pattern as tris(2,4,4-trimethylpentyl)phosphine oxide (R₃PO), which has been discussed in a previous paper.¹⁰ This compound can be recognized by the base peak at $m/z = 92$, which could be formulated as $[(CH_3)_2(CH_2)POH]^+$ and could be originated by three consecutive McLafferty rearrangements of the molecular ion. The compound presents a low intensity $[M^+ - 1]$ ion at $m/z = 385$. Other characteristic ions of this compound are those originated by fragmentation of the C-C bonds at the branching such as $[C_4H_9]^+$ ($m/z = 57$), $[M - CH_3]^+$ ($m/z = 371$), $[M - C_4H_9]^+$ ($m/z = 329$), $[M - C_5H_{11}]^+$ ($m/z = 315$) and $[M - C_8H_{17}]^+$ ($m/z = 273$).

Compounds 7 and 8 were not identified.

Figure 5b also shows that the monothiophosphinic acid is still present in the sample. This fact indicates that the mechanism of the decomposition of R₂P(S)SH leads to the formation of

Fig. 6 Mass spectra of (a) methyl ester of bis(2,4,4-trimethylpentyl)phosphinic acid (compound 1 in Fig. 5) and (b) tris(2,4,4-trimethylpentyl)phosphine oxide (compound 6 in Fig. 5b).

R₂P(S)OH as an intermediate product which is finally oxidized to R₂P(O)OH.

Conclusions

The study of the IR spectra of the rough extractants Cyanex 302® and Cyanex 301® has allowed to determine the most characteristic vibrational bands of their major components, bis(2,4,4-trimethylpentyl)monothiophosphinic acid and bis(2,4,4-trimethylpentyl)dithiophosphinic acid, respectively. The presence of other components of the commercial reagents has also been evidenced.

The IR spectra of the rough reagents after contact with 5 M HNO₃ have revealed that a 15-min shaking period followed by ten days of being the two phases on contact gives way to the complete oxidation of these thiono compounds to their corresponding oxo-analogues. A comparison of these spectra with that obtained for Cyanex 272® supported the postulated structures.

Gas chromatography with mass spectrometry detection has allowed us to determine that considerable decomposition occurs when dilute solutions of the reagents in toluene are shaken for 15 min with an equal volume of a 5 M HNO₃ solution. Thus, bis(2,4,4-trimethylpentyl)monothiophosphinic acid and tris(2,4,4-trimethylpentyl)phosphine sulfide are completely oxidized to bis(2,4,4-trimethylpentyl)phosphinic acid and tris(2,4,4-trimethylpentyl)phosphine oxide, respectively, whereas bis(2,4,4-trimethylpentyl)dithiophosphinic is partially oxidized to its monothio and phosphinic analogues.

The results obtained in this study indicate that Cyanex 302® is not suitable for the extraction of metal ions from an aqueous phase containing 5 M or more nitric acid since its major component, bis(2,4,4-trimethylpentyl)monothiophosphinic acid, has the drawback of being rapidly oxidized to bis(2,4,4-trimethylpentyl)phosphinic acid.

For Cyanex 301® care must be taken when using this

extractant in highly nitric acid media. Thus, low reagent concentrations should be avoided and its use has to be limited to the extraction of those metal ions that are extracted in one equilibration of only a few minutes. Contact with the aqueous phase should be limited to the period of phase equilibration as it has been demonstrated that the degradation of the organic phase occurs even in the absence of shaking. The mechanism of the decomposition indicates that its major component, bis(2,4,4-trimethylpentyl)dithiophosphinic acid, is partially oxidized to bis(2,4,4-trimethylpentyl)monothiophosphinic acid and bis(2,4,4-trimethylpentyl)phosphinic acid. These latter compounds would extract metal ions, but at higher pH values.

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