Hydrolytic and Radiolytic Degradation of Oφd(iB)Cmpo: Continuing Studies

K. L. Nash[a]; R. C. Gatrone[a]; G. A. Clark[a]; P. G. Rickert[a]; E. P. Horwitz[a]

[a] Chemistry Division, Argonne National Laboratory, Argonne, IL, USA

PLEASE SCROLL DOWN FOR ARTICLE

HYDROLYTIC AND RADIOLYTIC DEGRADATION OF OɸD(iB)CMPO: CONTINUING STUDIES

K. L. NASH, R. C. GATRONE, G. A. CLARK, P. G. RICKERT, and E. P. HORWITZ
Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA

ABSTRACT

The hydrolytic and radiolytic degradation of octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) in tetrachloro-ethylene (TCE) and in tributylphosphate-TCE mixtures (TRUEX process solvent) in contact with HNO_3 has been investigated. Gas chromatographic analysis of the degraded solutions has allowed identification and quantitation of a variety of organophosphorus degradation compounds derived from CMPO. The effect of degradation of the extractant solutions on the extraction and stripping of americium has been addressed, as has the effectiveness of Na_2CO_3 scrub procedures for restoring extractant performance. Extrapolation of these results to normal process application conditions indicates that neither hydrolysis nor radiolysis should compromise the americium extraction performance of TRUEX-TCE.

INTRODUCTION

The hydrolytic and radiolytic degradation of CMPO (octyl-(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide) has been reported in two prior reports from this laboratory (1,2). In the first of these investigations (1), the concentration of CMPO in degraded TRUEX process solvent (0.25 $\underline{M}$ CMPO - 0.75 $\underline{M}$ TBP-CCl_4) was calculated assuming third power extractant dependency in the decreasing distribution ratios for americium (D_{Am}) from 2.0 $\underline{M}$ HNO_3. The conclusion of that study was that CMPO apparently has

1355

considerable resistance to radiolytic degradation, as distribution coefficients did not decrease greatly with absorbed dose.

In the second study, the hydrolytic and radiolytic degradation of CMPO in CCl_4 (no TBP present) and in decalin was investigated (2). Capillary gas chromatography was used in the analysis of the degraded solutions to determine the concentration of CMPO at a given sample period, but detailed quantitative analysis of degradation products was not reported. Gas chromatographic analysis indicated that the actual concentration of CMPO was lower than the assumption of third power extractant dependency in D_{Am} suggested. It was shown that the degradation product methyl(octyl)-(phenyl)phosphine oxide ($MO\phi PO$) could partially replace CMPO in the extraction cycle to compensate for the reduced concentration of the primary extractant.

In view of our incomplete understanding of the system, we considered that further investigation of hydrolytic and radiolytic degradation of both CMPO and CMPO-TBP mixtures utilizing more specific quantitation of CMPO, TBP, and their degradation products by gas chromatographic and mass spectrometric analysis was indicated. In addition, CCl_4 has been replaced by tetrachloroethylene (TCE) in TRUEX flowsheet because of excessive evaporation of the former. As a result of the diluent change and the need for more complete quantitative data on rates and mechanism for CMPO degradation, we have completed a third investigation of this system.

Our objectives in this study are:

1. To identify and measure concentrations of CMPO and TBP hydrolytic degradation products in a biphasic system (the aqueous phase is nitric acid) under conditions which exceed the severity of presently anticipated applications.
2. To perform identical experiments in a radiation field.
3. To correlate hydrolysis and radiolysis results to identify probable degradation pathways for CMPO and to derive information on the rates and mechanisms of CMPO decomposition.
4. To correlate the concentrations of identified species with D_{Am} in degraded solvent.
5. To assess the effectiveness of aqueous sodium carbonate solutions as a solvent cleanup reagents.

EXPERIMENTAL

$O\phi D(iB)CMPO$ was purchased from M&T Chemicals, Inc. as an off-white, crystalline solid of nominal 98% purity. For most of the experiments this material was further purified by the MIX procedure (3) and then recrystallized from hexane. The resulting white crystalline material was shown by capillary gas chromatography and ^{31}P NMR spectroscopy to be greater than 99% $O\phi D(iB)CMPO$. Tri-

butylphosphate (TBP) was purchased from Eastman-Kodak as a 98% pure liquid and purified by the usual alkaline wash procedure. Tetrachloroethylene (TCE) was either Aldrich Gold Label or HPLC grade solvent. Nitric acid solutions were prepared in deionized water using Ultrex HNO_3.

Degradation studies were performed under the following set of conditions:

temperature = 50($\pm$0.1)°C
$[HNO_3]$ = 5.0 $\underline{M}$, 2.5 $\underline{M}$, 1.25 $\underline{M}$ (initial system total acidity)
initial volumes (each phase); 50 ml
equilibration time (hydrolysis); 12 weeks
irradiation dosage (radiolysis); 68 Wh/L.

The organic solutions investigated include:

0.25 $\underline{M}$ CMPO - TCE
1.0 $\underline{M}$ TBP - TCE
0.25 $\underline{M}$ CMPO - 1.0 $\underline{M}$ TBP - TCE (TRUEX process solvent).

These solutions were prepared by weighing the appropriate quantity of extractant and diluting to volume. Jacketed Pyrex reaction vessels were equipped with reflux condensers to minimize evaporative losses and were stirred with magnetic stir bars for intimate phase mixing. The irradiations were done in the ANL Chemistry Division ^{60}Co Irradiation Facility at a dose rate of 0.3 to 1.0 Mrad/hr. Absorbed dose was measured by cobalt glass dosimetry.

Hydrolysis experiments were run for 12 weeks with samples taken at two week intervals. Samples of the radiolyzed solutions were taken at 9.0, 16.0, 32.0, and 68.0 Wh/L total dose. At the sampling interval stirring was stopped to allow phase separation and 3-5 ml samples of the organic phase were taken. This sample was split into two equal portions. The portions were subjected to either water wash (to remove HNO_3) or 0.25 $\underline{M}$ Na_2CO_3 scrub followed by water wash (to remove HNO_3 and acidic degradation products). The scrub solutions were acidified with HNO_3 and the organic components extracted into $CHCl_3$. The $CHCl_3$ was subsequently evaporated off and the solids redissolved in a known volume of TCE. Aliquots of this solution were combined with an equal volume of the original washed solutions, diluted by a factor of 20, and derivatized with diazomethane (CH_2N_2) to convert acids to methyl esters required for gas chromatographic analysis. The scrub solutions were also derivatized and analyzed by gas chromatography. Separate aliquots of the non-derivatized organic solutions (without the scrub-extract portion of the solution) were used for the determination of D_{Am} from 0.01 $\underline{M}$ and 2.0 $\underline{M}$ HNO_3.

The capillary gas chromatographic analysis was done on a
Hewlett-Packard 5890 instrument equipped with a flame ionization
detector.   Peak integration was performed by a Hewlett Packard
3390A computing integrator.   The column was a 0.25 mm x 15 m fused
silica, DB-5 bonded phase column.   Helium was the carrier gas.
The chromatograph was run in the temperature program mode with the
program: 100°C for 1 minute, increased 10°C/minute to 260°C then
held at 260°C for 9 minutes.   Species were identified by compar-
ison of retention times with standards or by GC-MS.   Mass spectral
data were recorded on a Kratos MS 25 spectrometer at an ionization
voltage of 70 eV.   Gas chromatography-mass spectral data were
obtained using a Hewlett Packard Model 598 at 70 eV with speed
software.

In the analysis of degraded TRUEX solvent, an internal stan-
dard was found to be unnecessary as integrated areas from repli-
cate G.C. samples generally agreed to within <1% for TBP, and <2%
for CMPO.   Samples were compared with external standards solutions
of known (TBP) and (CMPO) in TCE and quantified by comparison with
the standard.   Mass balance for the analysis of CMPO and its
degradation products in TRUEX solvent was at least 97% and for TBP
>99% in the hydrolysis experiments.   In the radiolysis experi-
ments, mass balance was comparable to these values for low doses
but got progressively worse at higher doses.

Distribution ratios for americium between degraded solvents
and 0.01 $\underline{M}$, 2.0 $\underline{M}$ HNO$_3$ (to simulate stripping and extraction
stages in the process) were determined with tracer loading (^{241}Am)
of the samples.   The D$_{Am}$ values were determined in both the water-
washed and carbonate-scrubbed extractant solutions.   The analyti-
cal procedure was as previously described (2).

RESULTS AND DISCUSSION

Figure 1 is a reproduction of the capillary gas chromatogram
of TRUEX solvent at time zero, after 12 weeks hydrolysis, and
after 32.0 Wh/L irradiation.   While the same products are observed
in both radiolysis and hydrolysis experiments, the relative yields
of each differ.   The only identified products from TBP are dibutyl
phosphoric acid (HDBP) and relatively small amounts of monobutyl
phosphoric acid (H$_2$MBP).   A greater variety of degradation pro-
ducts is observed from CMPO.   Neutral products include methyl-
(octyl)(phenyl)phosphine oxide (MOϕPO) and octyl(phenyl)monoiso-
butyl CMPO (OϕM(iB)CMPO).   The acidic degradation products are
octyl(phenyl)phosphinic acid (H[O(ϕ)P]) and octyl(phenyl)phos-
phorylacetic acid (H[OϕPOAc]).   The probable interrelation of
these degradation products is shown in Figure 2.   This scheme is
consistent with those previously postulated except for the addi-
tion of the intermediate dealkylation step to form OϕM(iB)CMPO.
Separate experiments in which the degradation products MOϕPO and

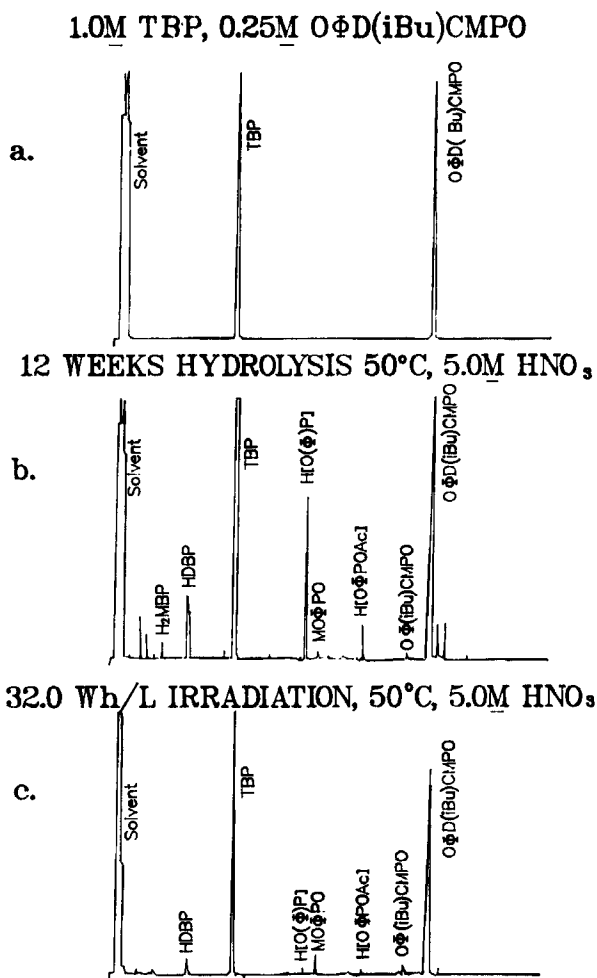## 1.0M TBP, 0.25M OΦD(iBu)CMPO

Fig. 1. Capillary gas chromatograms for TRUEX-TCE solutions (0.25 M CMPO, 1.0 M TBP in TCE): a. initial; b. after 12 weeks hydrolysis at 50°C in contact with 5.0 M HNO₃; c. after 32.0 Wh/L irradiation with ^{60}Co gamma rays at 50°C, 5.0 M HNO₃.
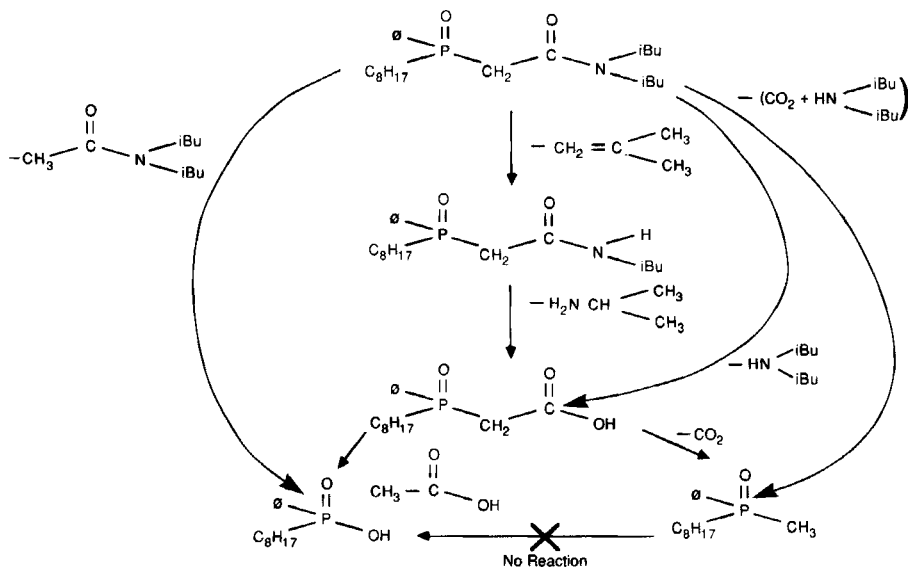
Fig. 2.   O φD(iB)CMPO degradation pathways.

H[O(φ)P] were contacted with 5.0 M HNO$_3$ for 6 weeks at 50°C indicated complete recovery of the starting materials, suggesting that they are terminal products and are not subject to further degradation under these conditions.

Hydrolysis: The summary of the chromatographic analyses for hydrolyzed TRUEX solvent is shown in Figure 3. The first order rate for formation of the acidic degradation products HDBP, H[O(φ)P], and H[OφPOAc] is high in the early stages of the experiment but decreases as the concentration of these species increases. No growth or decay of MOφPO was observed in the course of these experiments. The average concentration of MOφPO in the hydrolyzed samples is 0.0021 (±0.0016) M, representing less than 1% of the initial concentration of CMPO, in contrast to previously reported results for its degradation in CCl$_4$. Concentrations of both OφD(iB)CMPO and TBP appear to decrease linearly as a function of contact time.

In the respective single solute systems (i.e. CMPO-TCE, TBP-TCE), a much slower rate of decomposition was observed for both CMPO and TBP. Least-squares analysis of the data using a first order expression indicates that the rate of hydrolysis of CMPO is a factor of 4.3 faster in the mixed solute system; that for TBP is a factor of 7.5 faster. The increased rate of decomposition in
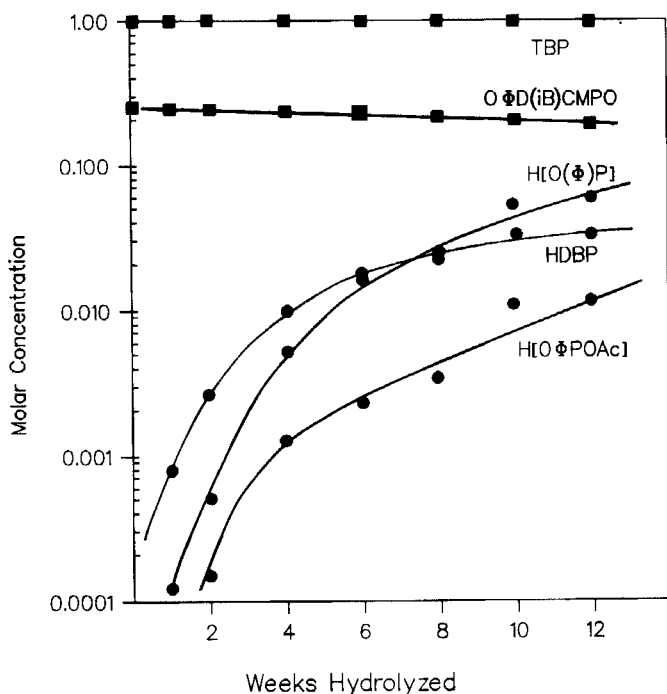
Fig. 3. Results of gas chromatographic analysis of hydrolyzed TRUEX-TCE solutions, T = 50°C, [HNO$_3$] = 5.00 M.

TRUEX process solvent is partly related to the organic phase [HNO$_3$] . The titrated nitric acid concentrations in the CMPO, TBP and TRUEX solutions (equilibrated with 5.0 M HNO$_3$) are 0.36 M, 0.89 M, and 1.02 M respectively. That the relationship is complex is shown by the observation that a 15% increase in [HNO$_3$] (1.02/0.89) results in a 7.5 fold increase in the rate of decomposition of TBP, but a 2.8 fold increase in [HNO$_3$] (1.02/0.36) is related to a 4.3 fold increase in CMPO degradation.

The effect of lower [HNO$_3$] on the product distribution and degree of decomposition of CMPO and TBP in TRUEX process solvent is shown in Figure 4. Both the rate of decomposition of CMPO and the relative yield of H[O(ϕ)P] increase dramatically at [HNO$_3$] > 2.5 M. The relative yield of HDBP, in contrast, increases at the lower nitric acid concentrations then levels off at [HNO$_3$] >2.5 M, presumably as a result of susceptibility of HDBP to further degradation to H$_2$MBP and H$_3$PO$_4$ at higher acidity.
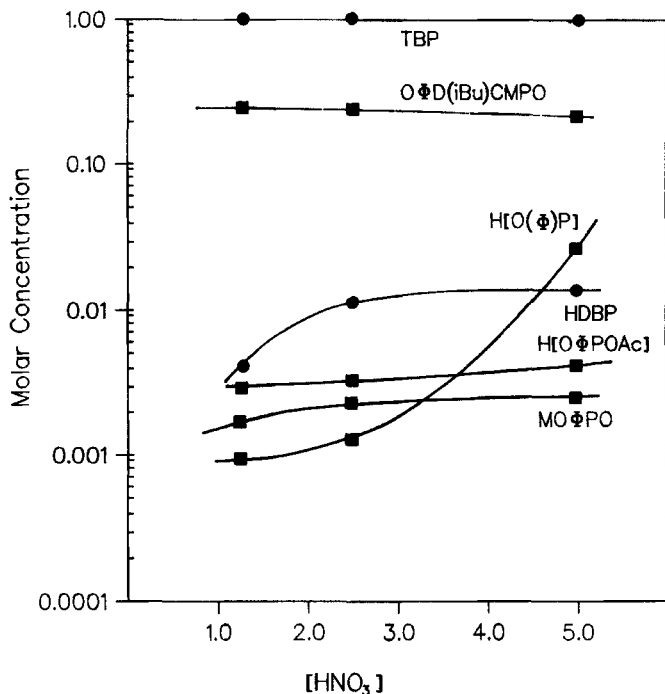
Fig. 4.   Results of gas chromatographic analysis of hydrolyzed
          TRUEX-TCE solutions at 50°C as a function of [HNO₃].

D_{Am} values for TRUEX extraction from 2.0 $\underline{M}$ and 0.01 $\underline{M}$ HNO₃
are shown in Figure 5.   The $D_{Am}^{2.0}$ values decrease with a less than
second order CMPO extractant dependency and are slightly increased
after   a   carbonate   scrub   of   the   solution.   The   reduced
stoichiometry in degraded solutions is in accord with previous
observations of this system (1,2). However, since MOφPO is not an
important degradation product, the previous explanation of partial
replacement of CMPO by MOφPO cannot apply in this case. The $D_{Am}^{0.01}$
values before and after carbonate washing indicate the deleterious
effect of acidic degradation products on TRUEX solvent performance
and the effectiveness of carbonate scrub in removing these pro-
ducts to restore the americium extraction performance of the
system.

Radiolysis: Gas chromatographic analysis of the samples from rep-
licate irradiations of TRUEX solutions at three different nitric
acid concentrations and as a function of dose are shown in
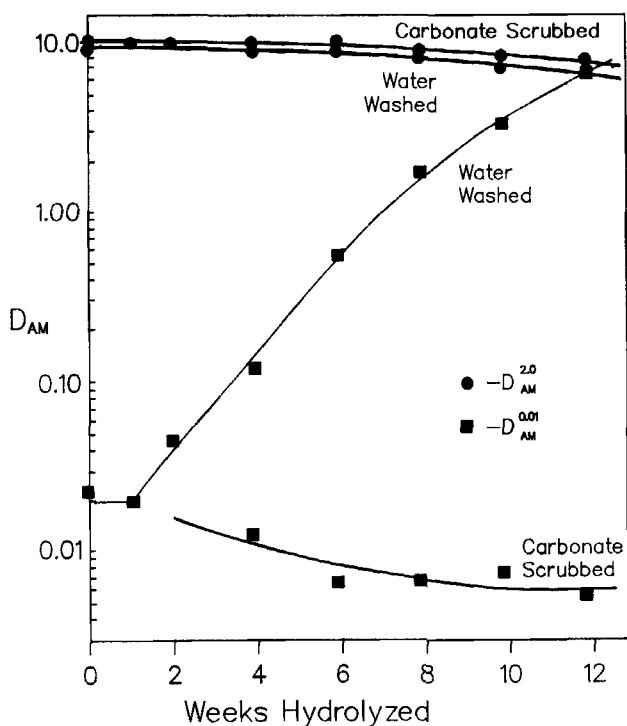Figure 6.   Irradiations of TBP-TCE and CMPO-TCE solutions gave

Fig. 5. Americium distribution ratios in hydrolyzed TRUEX-TCE solution before and after removal of acidic degradation products by carbonate scrub.

similar rates of decomposition and product distributions. Both CMPO and TBP mass balance are good at doses up to 18 Wh/L, but deteriorate with increasing dose to only 80% for CMPO and 90% for TBP at the maximum dose. The product distribution for those species identified in the GC analysis indicates HDBP as the principal TBP product and OϕM(iB)CMPO as the dominant product from CMPO.

G values (molecules/100 ev) for the rate of disappearance of CMPO and TBP were calculated from linear (zero-order) fits of the data (Table 1). The relative uncertainty in these values is acceptable and within the broad limits of previously published G values for TBP. The tabulated values suggest a possible slight improvement in radiation stability for CMPO and TBP in TRUEX solvent over the single solute systems. It also appears that CMPO has greater radiation stability in TCE than in CCl$_4$.
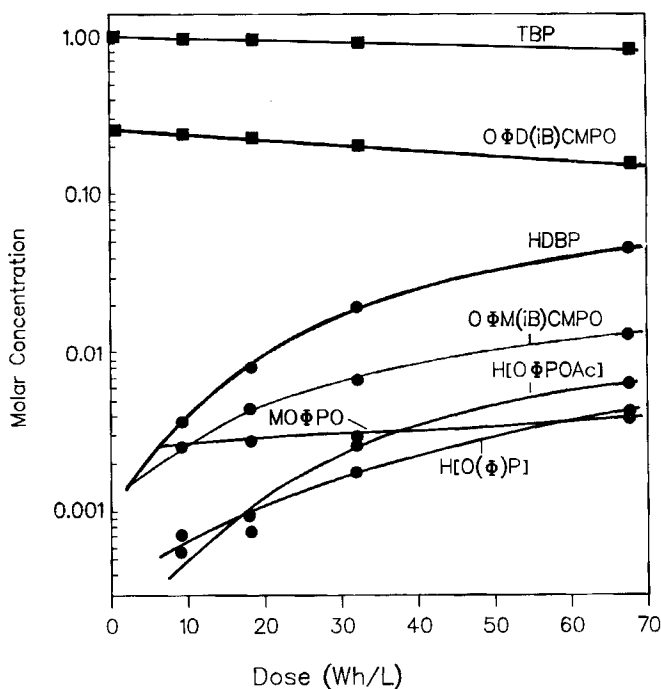
Fig. 6.   Results   of   gas   chromatographic   analysis   of   radiolysed
TRUEX-TCE solutions, T = 50°C, [HNO$_3$] = 1.25, 2.50, 5.00
M (average for irradiations of TRUEX-TCE in contact with
each).

Total acidity in each phase of the irradiated solutions, as
determined by indicator titration with standard NaOH, is given in
Table 2.   The overall increase in acidity is significant and found
primarily in the aqueous phase.   70-100% of the increase in aque-
ous acidity is due to HCl produced by the irradiation of TCE.   A
maximum of 7-10% of the aqueous acidity increase can be attributed
to H$_3$PO$_4$, H$_2$MBP, and HDBP.   60-90% of the increased acidity in the
organic phase is accounted for by the organic acids quantified in
the gas chromatographic analyses.

The phosphorus concentration in the aqueous phase accounts
for only 8-13% of the TBP and CMPO missing at high dose.   The
chromatograms of these highly irradiated solutions indicate the
presence of numerous unidentifiable (i.e., low concentration)
components, but total integrated intensity is insufficient to

TABLE 1.

G Values for Gamma Irradiation of TRUEX-TCE,

TBP-TCE, and CMPO-TCE

Solutions	Conditions	Yield	Ref.[*]
CMPO-TCE	5.0 M HNO$_3$, 0-32 Wh/L	G(-CMPO) = 5.21(±0.42)	pw.
CMPO-CCl$_4$	5.0 M HNO$_3$, 47-97 Wh/L	G(-CMPO) = 7.4(±1.4)	2
CMPO- TRUEX (TCE)	5.0, 2.5, 1.25 M HNO$_3$, 0-68 Wh/L	G(-CMPO) = 3.74(±0.36)	pw.
TBP-TCE	5.0 M HNO$_3$, 0-32 Wh/L	G(-TBP) = 9.2 (±3.0)	pw.
TBP- TRUEX (TCE)	5.0, 2.5, 1.25 M HNO$_3$ 0-68 Wh/L	G(-TBP) = 3.78(±0.63) G(HDBP) = 1.56(±0.08) G(total acid) = 18.0(±5.5) G(HCl) = 11.4(±2.0)	pw. pw. pw. pw.
30%TBP (CCl$_4$)	dry, 0.27-270 Wh/L	G(HDBP) = 18(±9)	4
TBP	neat-dry, 0.27-270 Wh/L	G(-TBP) = 5.5(±1)	4

pw.-present work

TABLE 2.

Titrated Acidity (Molar) for Irradiated TRUEX-TCE Samples

Sample ID	1.25 $\underline{M}$	2.50 $\underline{M}$	5.00 $\underline{M}$
blank, aq.	0.95	1.91	3.95
blank, or.	0.30	0.59	1.05
blank, total	1.25	2.50	5.00
68.0 Wh/L, aq.	1.36	2.10	4.42
68.0 Wh/L, org.	0.43	0.69	1.11
68.0 Wh/L, total	1.79	2.79	5.53
increased total	0.54	0.29	0.53
aqueous P[a]	0.016	0.011	0.012
HCl[b]	0.33	0.24	0.31
org. acids[c]	0.074	0.093	0.050

[a]Phosphorus in the aqueous phase by ICP analysis.
[b]Radiolysis product from TCE quantified gravimetrically by precipitation with Ag^+.
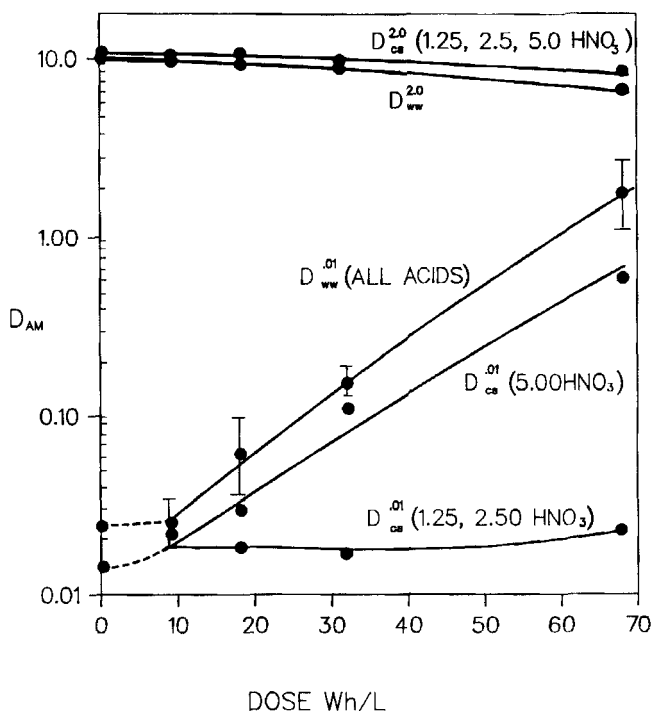[c]From gas chromatographic analysis.

Fig. 7   Americium distribution ratios in radiolysed TRUEX-TCE
solutions. $D_{Am}^{2.0}$ (carbonate scrubbed (CS) and water
washed (WW)) and $D_{Am}^{0.01}$ (WW) are average values for
solutions irradiated in the presence of 1.25, 2.50, and
5.00 $\underline{M}$ HNO_3. $D_{Am}^{0.01}$ (CS) values are for 5.00 $\underline{M}$ HNO_3 or
averages of 1.25 and 2.50 $\underline{M}$ HNO_3 as noted.

account for all of the missing CMPO and TBP. The missing material
may be polymeric species which do not exit the capillary column
under the analytical conditions, or volatile species which pass
through the column in the solvent peak. Previous investigations
of TBP radiolysis have reported both polymeric and gaseous
products (4).

Americium distribution ratios in the irradiated TRUEX solu-
tions are shown in Figure 7. The $D_{Am}^{2.0}$ and $D_{Am}^{0.01}$ values are the
average of results for TRUEX solutions contacted with the three
nitric acid solutions. Despite the destruction of nearly 40% of
the original CMPO in these samples after 68 Wh/L irradiation,
little decline is observed in $D_{Am}^{2.0}$. After carbonate scrub $D_{Am}^{2.0}$

TABLE 3.

Normalized Product Distribution for Degradation of CMPO at

68 Wh/L or 12 Weeks Hydrolysis

CMPO-TRUEX (TCE)

HYDROLYSIS	RADIOLYSIS
5.0 M HNO$_3$	
80% H[O(ϕ)P], 13% H[OϕPOAc], 8% MOϕPO	15% OϕM(iB)CMPO, 6% MOϕPO, 4% H[O(ϕ)P], 69% unknown
2.5 M HNO$_3$	
18% H[O(ϕ)P], 50% H[OϕPOAc], 32% MOϕPO	25% OϕM(iB)CMPO, 12% MOϕPO, 4% H[O(ϕ)P], 50% unknown
1.25 M HNO$_3$	
17% H[O(ϕ)P], 52% H[OϕPOAc] 30% MOϕPO	15% OϕM(iB)CMPO, 7% MOϕPO, 3% H[O(ϕ)P], 69% unknown

CMPO-TCE

HYDROLYSIS	RADIOLYSIS
5.00 M HNO$_3$	
40% MOϕPO, 50% H[OϕPOAc]	15% OϕM(iB)CMPO, 10% MOϕPO, 70% unknown
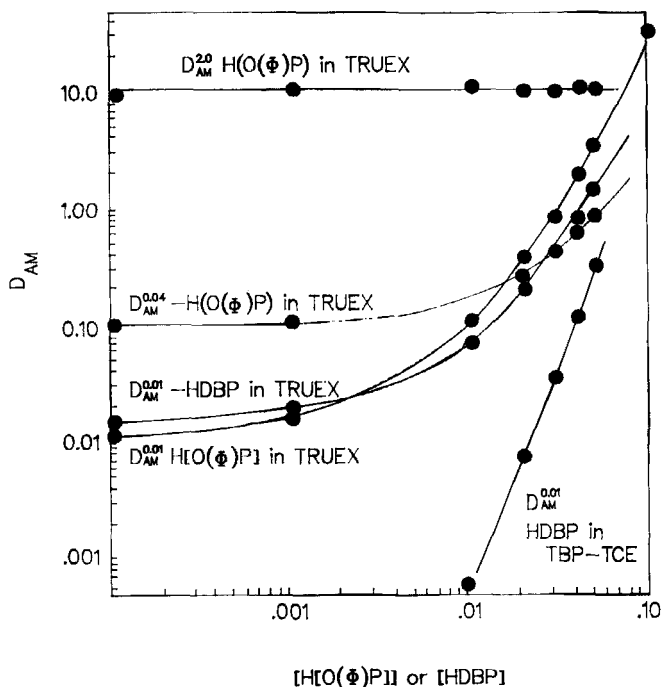
Fig. 8.   Americium distribution ratios in synthetic solutions.
          TRUEX is 0.25 $\underline{M}$ CMPO, 1.0 $\underline{M}$ TBP in TCE.

exhibits slightly less than first power dependence on [CMPO],
implying that an unidentified degradation product or some more
subtle alteration of the medium is acting to maintain D_{Am} approx-
imately constant.

        A rise is observed in $D_{Am}^{0.01}$ in these samples, though the
increase is less than was observed in the 12 week hydrolysis
experiments. This latter effect is probably the result of the
lowered yield of H[O(ϕ)P] in the irradiated solutions. The car-
bonate scrub procedure effectively lowers the $D_{Am}^{0.01}$ values in the
solutions which were equilibrated with 1.25 $\underline{M}$ and 2.5 $\underline{M}$ HNO$_3$, but
does not completely restore the $D_{Am}^{0.01}$ for the solution
equilibrated with 5.0 $\underline{M}$ HNO$_3$.

Correlation between hydrolysis and radiolysis: The normalized
yields (to 100% of degraded CMPO) of the various CMPO degradation
products are different for hydrolytic and radiolytic decomposition
and for CMPO-TCE vs. TRUEX-TCE (Table 3). The highest % yield of

TABLE 4.

H[O(φ)P], HDBP Distribution Ratios Between TRUEX-TCE

and Aqueous Carbonate Solutions

$[Na_2CO_3]$	$D(H[O(\phi)P])$	$D(HDBP)$
0.0625	0.012	<1E-4
0.125	0.013	7.4E-4
0.250	0.018	8.3E-4
0.500	0.018	3.9E-4

acidic degradation products occurs in TRUEX-TCE hydrolyzed with
5.0 M HNO_3, in which the organic phase concentration of HNO_3 is
greatest.   A decrease in $[HNO_3]$ lowers the relative yield of
H[O(φ)P] dramatically.   The $[HNO_3]$, however, does not effect the
distribution of products in the radiolytic degradation of CMPO.
Even absolute yields of identified radiolysis products of CMPO are
nearly identical in CMPO-TCE and TRUEX-TCE independent of the
nitric acid concentration.

It is reasonable to assume that the increase observed for
$D_{Am}^{0.01}$ is primarily a result of the presence of HDBP and H[O(φ)P]
in the degraded TRUEX solution.   Except for the solution radio-
lyzed in contact with 5.0 M HNO_3, removal of these acids by car-
bonate scrub restored low values for $D_{Am}^{0.01}$.   Figure 8 shows D_{Am}
values for synthetic solutions of H[O(φ)P] and HDBP in 0.25 M CMPO
- 1.0 M TBP-TCE.   At [H[O(φ)P]] or [HDBP] greater than 0.01 M,
$D_{Am}^{0.01}$ values increase with a second power extractant dependency.
Using these figures as calibration curves, D_{Am} values for degraded
TRUEX solvent were calculated as an algebraic mean of the expected
D_{Am} values for extraction by H[O(φ)P] and HDBP.   Agreement between
calculated and observed D_{Am} values was fair to good for both
hydrolyzed and radiolysed solutions.   Note also that at 0.04 M
HNO_3 (a probable acidity for back extraction under process
applications) the H[O(φ)P] extractant dependency for D_{Am} is
reduced to 1 or less.   At 2.0 M HNO_3, H[O(φ)P] has no influence on
D_{Am}.

In addition to investigations outlined above which suggest adequate removal of acidic degradation products by carbonate scrub under most conditions, we have determined the distribution ratios for H[O(ϕ)P], HDBP, and MOϕPO between TRUEX – TCE and aqueous carbonate solutions. The distribution ratios were measured by gas chromatographic analysis of derivatized samples of the organic solutions of the acids (after equilibration with aqueous Na_2CO_3 solutions), and $CHCl_3$ extracts of the acidified aqueous washes. Distribution ratios for HDBP and H[O(ϕ)P] were determined at 0.0625, 0.125, 0.250, and 0.50 $\underline{M}$ sodium carbonate, with results summarized in Table 4.

The distribution coefficient of each is low enough that two successive contacts with aqueous sodium carbonate solution will remove >99% of the material present. In contrast, MOϕPO is removed from 1 $\underline{M}$ TBP/TCE upon carbonate scrub by only a trivial amount as indicated by the measured distribution coefficient of 490($\pm$17) for $[Na_2CO_3]$ = 0.25 $\underline{M}$.

SUMMARY AND CONCLUSIONS

These results allow the following conclusions to be drawn:
1. Hydrolysis and radiolysis produce the same CMPO degradation products in different relative yields. Acidic degradation products are favored to a greater degree in hydrolysis and increase with the concentration of HNO_3. It is also noteworthy that both CMPO and TBP are degraded more severely by hydrolysis in TRUEX solvent that in either as a single solute system, but such differentiation is not observed in radiolysis of these same solutions. Irradiation of TRUEX-TCE to relatively high total dosage results in the production of unidentified CMPO degradation products.

2. The increase in D_{Am} at 0.01 $\underline{M}$ HNO_3 is due to the presence of both H[O(ϕ)P] and HDBP. In radiolyzed samples an additional unidentified component may affect $D_{Am}^{0.01}$ at high absorbed dose.

3. Contact with sodium carbonate solutions effectively removes major acidic degradation products and restores the original D_{Am} values of TRUEX-TCE process solvent in hydrolysed samples but is less effective in highly irradiated solutions.

4. The treatment received by these solutions in these experiments is more severe than the process solvent is likely to see under actual process applications (e.g., higher nitric acid concentration, 50°C, irradiation equivalent to 70 years exposure when used to decontaminate Pu scrap waste). Given the uncertainties in making extrapolations from limited information, it seems unlikely that either hydrolysis or radiolysis will have a significant deleterious effect on the americium extraction performance of TRUEX-TCE process solvent in any presently anticipated applications.

ACKNOWLEDGMENT

REFERENCES

1. Leonard, R. A., G. F. Vandegrift, D. G. Kalina, D. F. Fischer, R. W. Bane, L. Burris, E. P. Horwitz, R. Chiarizia, H. Diamond, Argonne National Laboratory Report ANL-85-45 (1985).
2. Chiarizia R. and E. P. Horwitz, Solvent Extr. Ion Exch. 4, 677-723 (1986).
3. Gatrone, R. C. , L. Kaplan, E. P. Horwitz, Solvent Extr. Ion Exch. 5(6), (1987).
4. Davis, Jr. W., "Radiolytic Behavior," in "Science and Technology of Tributylphosphate," Vol. 1, W. W. Schulz and J. D. Navratil, Eds., CRC Press Inc., Boca Raton, Florida, pp. 221-266 (1984).