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# Effects of Radiation, Acid, and Base on the Extractant Dihexyl-[(Diethylcarbamoyl) Methyl] Phosphonate

C. T. Bahner
R. R. Shoun
W. J. McDowell

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# EFFECTS OF RADIATION, ACID, AND BASE ON THE EXTRACTANT DIHEXYL-[(DIETHYLCARBAMOYL)METHYL] PHOSPHONATE

C. T. Bahner*
R. R. Shoun
W. J. McDowell

*Present address: Bluefield College, Bluefield, Va.

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
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## ABSTRACT

The effects of exposure to gamma radiation ($^{60}Co$) and of contact with acidic and basic aqueous solutions on dihexyl-[(diethylcarbamoyl)methyl]phosphonate (DHDECMP) were studied. Gamma radiation decomposes DHDECMP into a variety of products. The most troublesome of those are the acidic compounds that cause problems in stripping the actinides and lanthanides from the extractant at low acid concentrations. The rate of degradation of DHDECMP by radiation is about the same or only slightly higher than that of tri-n-butyl phosphate (TBP). It is relatively easy to remove the radiation-produced impurities by equilibration (scrubbing) with sodium carbonate or sodium hydroxide or by column chromatographic methods.

The hydrolysis of DHDECMP in contact with aqueous solutions containing less than 3 M $HNO_3$ is not more severe than that of TBP under the same conditions but is significant above that acid concentration. Hydrolysis of DHDECMP in contact with aqueous sodium hydroxide solution does occur, but it should not pose an important problem with the short contact times such as those anticipated for the removal of the radiation-induced degradation products by caustic scrubbing. The results of various chromatographic tests to characterize the degradation products of DHDECMP are also given.

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## 1. INTRODUCTION

A proposed process to scavenge traces of actinides from the acidic nitrate wastes generated in nuclear fuel reprocessing would utilize

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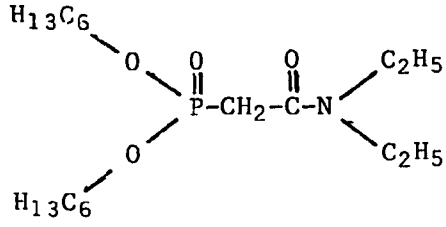
*Bluefield College, Bluefield, Va.

dihexyl[(diethylcarbamoyl)methyl]phosphonate DHDECMP)



and would entail exposure of the extractant to radiation and contact with nitric acid solutions, and may also involve contact with alkaline solutions in the extractant clean-up steps. Exposure to these environments could result in degradation of DHDECMP by radiolysis or by hydrolysis, either at an ester group or at the amide group. In addition to destruction of the extractant, organic-soluble acid phosphates with cation exchange properties may be produced whose presence will prevent effective stripping of the actinides by water or dilute acids. Such a compound, hexyl hydrogen [(diethylcarbamoyl)methyl]phosphonate, has been identified as the cause of stripping difficulties in unpurified DHDECMP.[1]

Reid[2] noted that amides were hydrolyzed more rapidly by alkali than acid at the same concentration. Christol and Marty[3] reported that the alkaline hydrolysis of the first ester group in dimethyl phosphonate is 10 times as rapid as the first stage hydrolysis of trimethyl phosphate, but the second stage is very slow. Hudson and Keay[4] reported that the hydrolysis of diethylmethyl phosphonate was many times more rapid in alkaline as in acid medium. They suggested an SN 2 type mechanism for alkaline conditions involving an intermediate activated complex and an SN 1 type reaction for acid conditions. Alkaline hydrolysis is 15 times faster for a methoxy group than for an ethoxy group, but the rates for the two groups are about the same in acid hydrolysis. Cherbuliez, Hunkeler and Rabinowitz[5] reported that in a solution containing HCl equivalent to 1 mol of hydrogen ion per liter (1 N* HCl) primary phosphonic esters are hydrolyzed more rapidly than primary phosphoric esters,

*The symbol N will be used throughout this report to indicate an amount of a substance chemically equivalent to a mole of hydrogen ion per liter of solution. Similarly the symbol M will be used to indicate a quantity of one mole of a substance per liter of solution.

but more slowly than the secondary phosphoric esters. In 1 N NaOH at 100°C, the primary phosphonic esters hydrolyze slowly ($t_{1/2}$ >50 h) and are more stable than the secondary phosphoric esters. (Secondary phosphoric esters are more rapidly hydrolyzed by acid or alkali than are the phosphoric monoesters.) Phosphonic monoesters are hydrolyzed more rapidly in acid than in alkaline solution, least rapidly at about pH 4.5. The stability of DHDECMP in the presence of amines is also of interest because amines are produced by radiolysis and hydrolysis and because of the possibility of using amines to remove acid impurities. Billman, Radike and Mundy[6] reported alkylation of aromatic amines by heating with a trialkyl phosphate.

Schulz and McIsaac[7] have reported the effects of radiolysis of 15 vol % DHDECMP in trichlorobenzene containing 0.5 M $HNO_3$ and 0.028 to 0.236 g/L of $^{241}Am$. The products formed included an acidic species with great affinity for both Am(III) and Pu(IV). They suggest that this behavior is similar to that of tri-n-butyl phosphate (TBP) which forms dibutylphosphoric acid. Radiolysis of TBP has been investigated extensively.[8-11] Hydrogen and, to a smaller extent, hydrocarbons are found as gaseous radiolysis products of TBP, but dibutyl phosphate (DBP) appears to be the product of greatest concern. By analogy, DHDECMP would be expected to yield hexyl[(diethylcarbamoyl)methyl]phosphonic acid (HDECMP) as a major product. On the other hand, DHDECMP contains an amide group which is also subject to attack. Rogers, Bolte, and Rao[12] concluded from a study of aliphatic amides that "An alkyl substituent on nitrogen is the most favored site for loss of a proton... It is the C-H bond adjacent to the nitrogen atom or the carbonyl group which is preferentially broken."

The exploratory studies reported in this paper are intended to identify problems of radiolysis and hydrolysis (and possible related aminolysis) that may be encountered in the use of DHDECMP as an extractant, to determine their relative magnitude, and to provide data useful in the engineering planning of an extraction process with this reagent.

## 2. EXPERIMENTAL

The DHDECMP was obtained as a special preparation from Wateree Chemical Co., Lugoff, S. C. It was purified by molecular distillation at 0.4 Pa (3 microns) and 58°C, washing with aqueous sodium carbonate and drying under reduced pressure. Elemental analysis of the purified material gave C, 59.48%; H, 10.51%; N, 3.74%; theoretical, C, 59.50%; H, 10.47%; N, 3.86%.

The effects of nitric acid and sodium hydroxide were studied by the two-phase equilibration of DHDECMP, both undiluted and in solution in diethylbenzene (DEB), with various concentrations of nitric acid and of sodium hydroxide at room temperature or at elevated temperatures in a water bath.

The reaction of DHDECMP with diethylamine was carried out by heating a mixture of the two substances in a constant temperature glycol bath under a reflux condenser. At the end of the reaction time, excess amine was removed in a rotating evaporator at 2 kPa (15 mm), and the residue was dissolved in a large volume of hexane. The acid was extracted with standard 1.0 N NaOH, and the amine was extracted with 1.0 N HCl. The quantities were estimated by back titration.

Two cobalt sources were used for the irradiations. The cobalt source described by Davis[13] was used early in the work; later a Shepherd Model 109* irradiator (nominal 24,000 Ci) was used. The samples were irradiated in glass containers held in the center of the inner cavity; temperatures were 40 and 46°C for the older and new units respectively. The radiation exposure was calculated from the data supplied by Davis[13] or by the operation manual for the Shepherd irradiator together with the recalibration by W. D. Arnold of this laboratory, corrected for radioactive decay.

Small weighed samples of DHDECMP were irradiated in sealed 5-ml glass containers in order to study the gaseous irradiation products. After irradiation, the bulb was connected to a gas chromatograph or a mass spectrograph. Rough estimates of the gas pressure were obtained, and the chief products which were not retained in the liquid at room temperature were identified.

*J. L. Shepherd and Associates, Glendale, Calif.

Acid-base titrations were carried out with the aid of a pH meter or a Metrohm E536 Potentiograph using ethanol or ethanol-water mixtures. The "pH" values observed in the alcoholic solutions were not true pH values, but provided a useful arbitrary reference scale. For comparison, titration curves of strong and weak acids and amines and amine salts in 100% and 50% ethanol were prepared. Because of the small quantities of radiolysis products available, many of the titrations were carried out on a semi-micro scale using 1.000 ml or less of 0.0400 N NaOH in ethanol or 0.0550 N $HClO_4$ in dioxane.

Distribution ratios were measured by shaking two immiscible liquids containing a small amount of solute thirty minutes or longer, allowing the layers to separate, centrifuging if necessary, and analyzing the equilibrated phases.

## 2.1 EUAM Test

This test, based on the assumption that the $Am^{3+}$ and $Eu^{3+}$ are complexed equally, rapidly, and strongly, evaluates the effectiveness in extracting trivalent actinides by measuring the quantity of $Eu^{3+}$ held by the extractant at loading. A 10-mg sample of extractant in 1.00 mL of DEB is equilibrated with 1.00 mL of 0.001 M $HNO_3$ containing 0.001 or 0.002 M $Eu(NO_3)_3$ spiked with a small amount of $^{241}Am$. Aliquots of one or both layers are analyzed, and the number of milli-equivalents held in the organic layer per gram of chelating agent is calculated and recorded as the EUAM value. Some fractions tested tended to form precipitates with $Eu^{3+}$ or to form a gel or third phase; therefore, the result is only approximate in these cases. Nevertheless, the test is helpful in seeking the most active fractions as regards the extraction of trivalent elements.

## 2.2 AM Test

This is an empirical extraction test used to indicate the presence of the undesirable impurity responsible for the retention of americium when the organic phase is stripped at a low aqueous acidity. A 6 N $HNO_3$ solution containing $^{241}Am$ tracer is equilibrated with an equal volume of a 30 vol % solution of the extractant in DEB, and an aliquot of each layer

is taken for gamma or alpha counting. The ratio of net counts per minute in the organic phase to that in the aqueous phase is recorded as the $AM^1$ value. The count ratio after the first wash of the organic phase with an equal volume of stripping solution (water or dilute 0.1 M nitric acid) is the $AM^2$ value, and the ratio after the second wash with an equal volume of water is the $AM^3$ value.

### 2.3 Thin-Layer Chromatography

Standard commercial (Eastman) silica gel plates were used, and the chromatogram developed by placing the strip in a 1-L bottle containing a small amount of solvent. The solvents most often used were benzene and mixtures of benzene with methanol or ethanol, acetone, and methanol. The solvent front was allowed to advance about 10 cm past the upper edge of the original spot; then the strip was dried and examined by ordinary light, by ultraviolet light of two different wavelengths, 254 and 365 nm, and finally by exposure to iodine vapor in order to reveal spots not detected by the other methods. Thin-layer chromatography was extensively used as a qualitative test and as a guide to setting up column chromatographic procedures.

### 2.4 Column Chromatography

Columns of BioSil A,* a silicic acid material, were used to remove impurities from small samples of DHDECMP and to fractionate impurities. BioSil A, -74 + 44 μm (+ 200-325) mesh, suspended in benzene ($C_6H_6$) was used to form a column in a 1-cm tube. The sample to be separated was placed on the column as a solution in 10 to 50 times its volume of benzene because attempts to introduce an undiluted sample onto the column produced unsuccessful results. Elution was achieved with pure benzene followed by increasing concentrations of methanol ($CH_3OH$) or ethanol ($C_2H_5OH$) in benzene. Final stripping was effected with a pure alcohol. The effluent was collected in small weighed beakers or bottles, and the solvent was removed by evaporation at atmospheric pressure followed by vacuum drying at 130 Pa ( <1 mm Hg).

*Bio-Rad Laboratories, Richmond, Calif.

For removal of impurities from irradiated DHDECMP, a 2-g sample in 100 mL of benzene containing 2% methanol was applied to a 21-cm-high column and eluted with the same solvent.

In some experiments, Cellex-D,* diethylaminoethyl cellulose (capacity, 0.70 meq/g) was used instead of silicic acid with pure benzene as the solvent. An initial contact time of 20 min was allowed to fix the sample on the column. The DHDECMP was eluted rapidly from this column with pure benzene.

### 2.5 Amine Test

Selected samples were tested for the presence of amine salts by mixing a small drop of the sample with a drop of 1 N NaOH in a small vial and then testing the air in the vial for amine vapor by use of moist indicator paper. Odor often assisted in confirming the test.

Amine analyses by the ORNL Analytical Chemistry Division were carried out on a semi-micro scale by making the sample strongly alkaline with sodium hydroxide and distilling the volatile amine into an acid solution, as in the Kjeldahl analysis, followed by back titration. Carbon, hydrogen and nitrogen analyses on approximately 1-mg samples were run on a Perkin-Elmer Model 240 Elemental Analyzer by the ORNL Analytical Chemistry Division.

## 3. RESULTS

### 3.1 Effects of Nitric Acid

#### 3.1.1 Diluent

Diethylbenzene, often suggested as a diluent for DHDECMP in a solvent extraction process, developed a bright yellow color when shaken for 10 to 12 days with 4 or 6 N $HNO_3$ at 40°C. Although this indicates a chemical change, the extraction behavior of a solution of DHDECMP prepared with the nitric acid–treated solvent was normal, except that phase separation appeared slower than usual. The yellow color was not produced by 2 N $HNO_3$.

*Bio-Rad Laboratories, Richmond, Calif.

### 3.1.2 Acid extraction by DHDECMP

A 1.00 M solution of DHDECMP in DEB extracted significant quantities of acid when equilibrated with various concentrations of nitric acid (Table 1).

Table 1. Distribution of nitric acid between water and 1.0 M DHDECMP in diethyl benzene

| Temp (°C) | $HNO_3$ conc (M) | | Organic |
|---|---|---|---|
| | Aqueous | Organic | Aqueous |
| 25 | 1.54 | 0.46 | 0.29 |
| 25 | 3.1 | 0.90 | 0.29 |
| 25 | 4.72 | 1.28 | 0.27 |
| 40 | 3.67 | 0.90 | 0.24 |

Washing with water removed the nitric acid readily. For example, when 1 mL of 1.0 M DHDECMP in DEB containing 0.90 meq $HNO_3$ was washed with 5 volumes of water, 0.81 meq of the acid was removed. A second wash with a similar volume of water removed an additional 0.06 meq.

### 3.1.3 Evidence for possible acid hydrolysis

Equilibrations of 1.0 M DHDECMP in DEB with three different concentrations of $HNO_3$ were made at 40°C by vigorous agitation for 15 d with 2.0 and 6.0 M $HNO_3$ and for 12 d plus 8 d standing with 3.1 M $HNO_3$. The DHDECMP solution equilibrated with 2.0 M $HNO_3$ contained approximately 0.50 meq/mL of acid total. This is within experimental accuracy of the amount of nitric acid extracted by the DHDECMP (Table 1) and suggests no appreciable hydrolysis. With 3.1 M $HNO_3$, however, 0.16 meq/mL of weak acid (similar in strength to dihexyl phosphoric acid) and $\sim$0.04 meq/mL of a weaker acid (like benzoic or sebacic) were found in the organic phase after it had been washed with an equal volume of water three times. If we assume the water washes removed all the nitric acid, and the acid titrated was a monobasic acid resulting from hydrolysis, this suggests approximately 16% of the reagent was hydrolyzed. Contact with 6 M $HNO_3$ produced

approximately 0.35 meq/mL of the weak acid; this implies that about 35% of the DHDECMP was hydrolyzed based on the above assumptions.

In order to provide some comparison, the rate of hydrolysis of TBP dissolved in 3 M $HNO_3$ is said to result in about a 5% loss of TBP in 12 d at 25°C;[15] however, much increased hydrolysis rates have been indicated in a two-phase system.[14] Thus, the rate of hydrolysis of DHDECMP by nitric acid appears equal to or somewhat greater than that of TBP.

After equilibrating 6 N $HNO_3$ and DHDECMP as described previously, the aqueous phase was found to contain 0.102 meq of amine per millimole of DHDECMP used, whereas only a trace of amine was found in the aqueous phases from the experiments with 2.0 and 3.1 M $HNO_3$.

Entries 18 and 19 in Table 2 and entries 5, 6, and 7 in Table 3 indicate that nitric acid hydrolysis has a small but measurable effect on the ability to strip americium and little effect on the loading of DHDECMP.

Further, after equal volumes of 6 N $HNO_3$ and undiluted DHDECMP had been shaken together for 60 h at room temperature, the aqueous layer did not give any amine odor on addition of NaOH; however, after equal volumes of 2 N $HNO_3$ and undiluted DHDECMP had been shaken for 22 d, a strong amine odor was detected on addition of an excess of NaOH to the aqueous layer. These results suggested the slow hydrolysis of DHDECMP by $HNO_3$ as dilute as as 2 N.

### 3.2 Effects of Alkali

After shaking 0.294 g (0.81 mmol) of undiluted DHDECMP with 10.0 mL of 0.100 N NaOH for 10 d, titration of the remaining base with HCl indicated that 0.10 meq of acid had been produced. After similar contacts, 2.0061 mmol of DHDECMP and 1.00 mL of 0.10 N NaOH required only 0.015 meq of HCl in a two-phase titration to reach an aqueous phase pH of 8 or 0.0525 meq to reach pH 4.5, and 2.0065 mmol of DHDECMP with 1.00 mL of 0.500 N NaOH required 0.015 meq of HCl to reach pH 8 or 0.165 meq of HCl to reach pH 4.5. This suggested that 0.085 and 0.485 meq of acid, respectively, had been formed. In other words, in the last two experiments where the DHDECMP was in large excess, hydrolysis of the ester or amine had continued until only a very small concentration of free NaOH remained.

Table 2. EUAM Binding

| Expt No. | DHDECMP sample treatment | Total material (mg/mL) | Am conc (counts/s) | | $D_{Am}$[c] | EUAM value (mmol Eu/g DHDECMP) |
|---|---|---|---|---|---|---|
| | | | Aq[a] | Org[b] | | |
| 1 | Molecular distillation | 95 | 3391 | 3.7 | 0.0011 | |
| 2 | Molecular distillation, wash twice with 1 N $Na_2CO_3$, and then water | 95 | 3343 | 0.3 | 0.0001 | |
| 3 | As in 2 and irradiated to $1.6 \times 10^8$ rads | 95 | 2670 | 665 | 0.25 | 0.021 |
| 4 | As in 3 | 95 | 1836 | 1113 | 0.61 | Am only, no Eu |
| 5 | As in 3 and processed through a Cellex-D column | 95 | 3110 | 196 | 0.063 | |
| 6 | As in 3 and processed through a 15-cm-long Biosil A column; chief fraction | 95 | 3303 | 5.6 | 0.0017 | |
| 7 | As in 6; 11th fraction | 8 | 1883 | 1226 | 0.65 | 0.51 |
| 8 | As in 3 and processed through a 21-cm-long Biosil A column; fraction 103-I (main) | 10 | 3058 | 1.1 | 0.0004 | |
| 9 | As in 8; fraction 103-II (7%) | 10 | 3025 | 5.6 | 0.0018 | |
| 10 | As in 9; fraction 103-III (9%) | 10 | 2537 | 531 | 0.209 | 0.17 |
| | Fraction 103-III processed through a 30-cm-long Biosil A column | | | | | |
| 11 | Fraction M | 7.7 | 2983 | 141 | 0.047 | |
| 12 | Fraction U | 9.3 | 3057 | 78 | 0.026 | |
| 13 | Fraction W | 17.6 | 2415 | 657 | 0.272 | |
| 14 | $CH_3OH$ column strip | 12.9 | 884 | 2273 | 2.57 | 0.77 |
| 15 | As in 2, irradiated to $3.1 \times 10^8$ rads and processed to recover acidic materials; fraction 126-Pr | 10 | 1788 | 1354 | 0.76 | 0.43 |
| 16 | As in 15; fraction 127-A | 10 | 2517 | 523 | 0.21 | 0.12 |
| 17 | As in 16; fraction 127-B | 10 | 2727 | 386 | 0.14 | 0.12 |
| 18 | As in 1 and 22-d contact with 2 N $HNO_3$ | 95 | 3280 | 5.6 | 0.0017 | |
| 19 | As in 1 and 22-d contact with 6 N $HNO_3$ | 95 | 3286 | 10.9 | 0.0033 | |

[a] Aq: concentration of $^{241}Am$ in aqueous phase.

[b] Org: concentration of $^{241}Am$ in organic phase.

[c] Org/Aq.

Table 3. Effects of impurities on stripping from DHDECMP solutions

| Expt. No. | Material | Loading[a] Aq[b] | Loading[a] Org[c] | Loading[a] $D_{Am}$[d] | First strip 0.1 M $HNO_3$ Aq[b] | First strip 0.1 M $HNO_3$ Org[c] | First strip 0.1 M $HNO_3$ $D_{Am}$[d] | Second strip 0.1 M $HNO_3$ Aq[b] | Second strip 0.1 M $HNO_3$ Org[c] | Second strip 0.1 M $HNO_3$ $D_{Am}$[d] | Third strip 0.01 M $Eu(NO_3)_3$-0.1 M $HNO_3$ Aq[b] | Third strip 0.01 M $Eu(NO_3)_3$-0.1 M $HNO_3$ Org[c] | Third strip 0.01 M $Eu(NO_3)_3$-0.1 M $HNO_3$ $D_{Am}$[d] | EUAM value (mmol Eu/g DHDECMP) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Purified 1.0 M DHDECMP in diethyl benzene | 71 | 926 | 13.0 | | | | | | | | | | |
| 2 | Purified 1.0 M DHDECMP irradiated to $3.08 \times 10^8$ rads | 139 | 1906 | 13.7 | 226 | 1726 | 7.6 | 118 | 1618 | 13.7 | 955 | 536 | 0.56 | 0.48 |
| 3 | Irradiated DHDECMP (expt 2) dissolved in benzene and processed through a Biosil-A column | 242 | 1772 | 7.3 | 962 | 1085 | 1.57 | 729 | 340 | 0.07 | 305 | 51 | 0.17 | 0.0017 |
| 4 | Irradiated DHDECMP (expt 2) dissolved in hexane and treated with 1 N NaOH | 212 | 1724 | 8.13 | 684 | 1088 | 1.59 | 818 | 274 | 0.33 | 248 | 24 | 0.10 | 0.0011 |
| 5 | 1.0 M DHDECMP in diethyl benzene after shaking with 4.0 M $HNO_3$ for 10 d at 40°C | 146 | 1852 | 12.7 | 528 | 1329 | 2.52 | 834 | 443 | 0.53 | 364 | 76 | 0.21 | 0.0017 |
| 6 | 1.0 M DHDECMP in diethyl benzene after shaking with 6.0 M $HNO_3$ for 10 d at 40°C | 221 | 1796 | 8.1 | 562 | 1257 | 2.24 | 226 | 1022 | 4.5 | 580 | 265 | 0.46[e] | 0.4013[f] |
| 7 | Diethyl benzene shaken with 6.0 M $HNO_3$ for 10 d at 40°C before preparing 1.0 M DHDECMP solution | 123 | 1452 | 11.8 | 506 | 983 | 1.9 | 790 | 194 | 0.25 | 183[g] | 17[g] | 0.09[g] | |
| 8 | 1.0 M DHDECMP in diethyl benzene irradiated 8 weeks while in contact with 2 M $HNO_3$; (DHDECMP irradiated to $1.5 \times 10^8$ rads). | 130 | 1615 | 12.4 | 337 | 1364 | 4.0 | 390 | 1000 | 2.6 | 576 | 1.3 | 0.0006 | |

[a] Unless otherwise indicated, a 30 vol % solution of the material listed was shaken with an equal volume of 6 M $HNO_3$ spiked with $^{241}Am$.

[b] Aq: Concentration of $^{241}Am$ in aqueous phase (counts/s).

[c] Org: Concentration of $^{241}Am$ in organic phase (counts/s).

[d] $D_{Am}$ = Org/Aq.

[e] Third strip with 0.01 M $HNO_3$ gave Aq 25, Org 1037, and $D_{Am}$ 41. Fourth strip with 0.01 M $HNO_3$ gave Aq 20, Org 980, and $D_{Am}$ 49. These runs were made before final strip with $Eu(NO_3)_3$.

[f] Final strip contained 0.04 M instead of 0.01 M $Eu(NO_3)_3$.

[g] The third strip was made with 0.1 M $HNO_3$.

A mixture of 4.00 g DHDECMP (11.0 meq) with 2.00 mL of 1.00 N NaOH became homogeneous and crystal clear after shaking 40 h at 28°C. After a total of 8 d shaking, only 0.045 meq of acid was required to neutralize the remaining free NaOH. The mixture was acidified with 2.3 mL of 1.00 N HCl and diluted with more water which caused separation of a 4.4 mL oil layer. The water layer was found to contain 0.15 meq of amine, suggesting that about 7% of the NaOH had been consumed in hydrolysis of the amine linkage in the DHDECMP and about 90% in hydrolysis of a $C_6H_{13}OP$ group. Similarly, a mixture of 4.00 g of DHDECMP and 10.0 mL of 1.00 N NaOH became homogeneous and clear after 6 d of shaking. After acidification with HCl and dilution with water, the aqueous layer contained 0.30 meq of amine and the oil layer 6.2 meq of acid, presumed to be largely organic acids formed by hydrolysis of the DHDECMP. These results suggest that prolonged contact of DHDECMP with caustic solutions will produce serious amounts of hydrolysis.

### 3.3 Effects of Diethylamine

Since diethylamine appears to be formed both by hydrolysis and radiolysis of DHDECMP, the reaction of the amine with DHDECMP is a matter of interest. The possibilities exist that (1) the reaction of excess diethylamine with impure or degraded DHDECMP might reverse the hydrolysis reaction,

$$(C_6H_{13}O)_2\overset{O}{\overset{\|}{P}}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + HN(C_2H_5)_2 \rightarrow (C_6H_{13}O)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}N(C_2H_5)_2 + H_2O,$$

or (2) diethylamine, being a base, might contribute to and speed the degradation of DHDECMP. We were able to test the second of these possibilities.

Heating DHDECMP for 76 h with a large excess of refluxing (55.5°C) diethylamine produced a water-insoluble acid in a yield of about 5%. If only 2 mol of amine were used per mol of DHDECMP, a higher temperature was attained, and after heating for 10 d, the yield of organic acid was about 12% and that of a heavy amine about 13%. Thus, heating 0.042 mol (15.2 g) of DHDECMP with 0.083 mol (6.1 g) of diethylamine for 72 d

produced a reaction mixture from which 0.012 mol (1.85 g) of N,N-diethyl-N-hexylamine [equiv wt, 157 (theoretical, 157); refractive index, $\eta_D^{20}$, 1.4270, (lit.[16] $\eta_D^{20}$ = 1.4245)] was recovered. The total amount of acid produced by this reaction was estimated to be 9 g. Further purification by extraction yielded a fraction with an equiv wt of 294 (theory for pure HDECMP = 279). Though not perfectly pure, this sample served to obtain useful distribution ratios (Table 4). These data suggest that HDECMP can be easily scrubbed from an aliphatic diluent by water.

Table 4. Distribution of HDECMP[a] between organic solvents and water

| Organic solvent | HDECMP concn (N) | | Organic / Aqueous |
|---|---|---|---|
| | Organic | Aqueous | |
| Benzene | 0.022 | 0.021 | 1.0 |
| Benzene | 0.007 | 0.014 | 0.5 |
| Hexane | <0.0007 | 0.044 | <0.016 |
| 2-ethyl-1-hexanol | 0.068 | 0.010 | 6.8 |

[a]Hexyl[(diethylcarbamoyl)methyl]phosphonic acid.

A 1.0-g sample of the crude brown oil obtained by refluxing DHDECMP with diethylamine followed by diluting the mixture in hexane, extracting this solution with 1.0 M NaOH, and acidifying the resulting aqueous phase with an equal amount of 1.0 N HCl was chromatographed to produce the fractions shown in Fig. 1. Elemental analyses (% N, % C, and % H) of a fraction are shown above the bar representing the relative weight of that fraction. A 1.35-g sample obtained by benzene extraction from the above acidified aqueous solution was chromatographed to produce the fractions shown in Fig. 2. The equivalent weight and the milli-equivalents per gram of sample in two "pH" ranges are shown for selected fractions.

### 3.4 Effects of Radiation

Purified DHDECMP, which is an almost water white liquid, begins to evolve small bubbles after a short period of irradiation. If

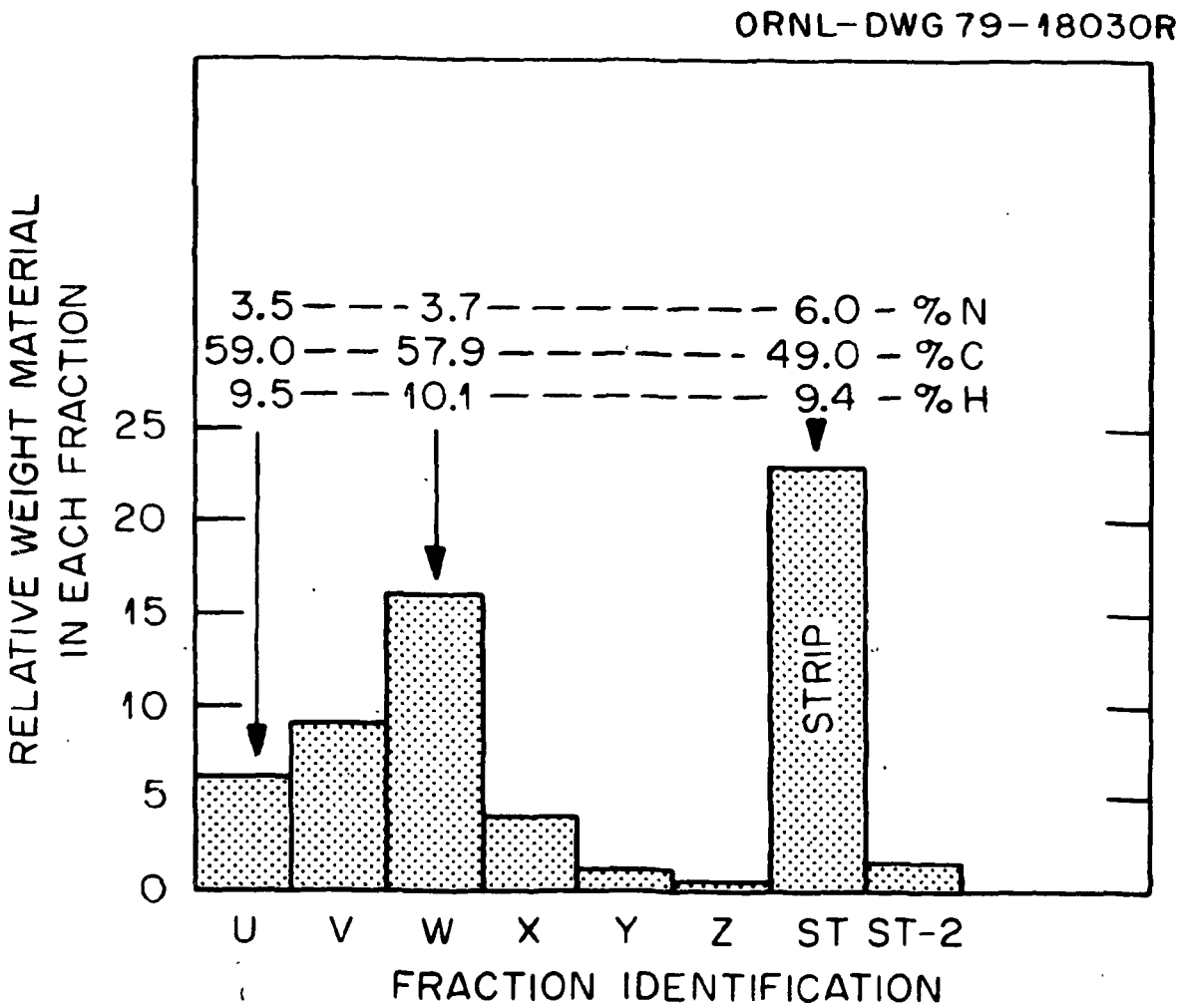



Fig. 1. Column chromatography of the oil obtained by the acidification of the aqueous alkaline extract from the DHDECMP — diethylamine reaction mixture (sample 147). Relative total weight of material obtained for equal volumes of eluate.

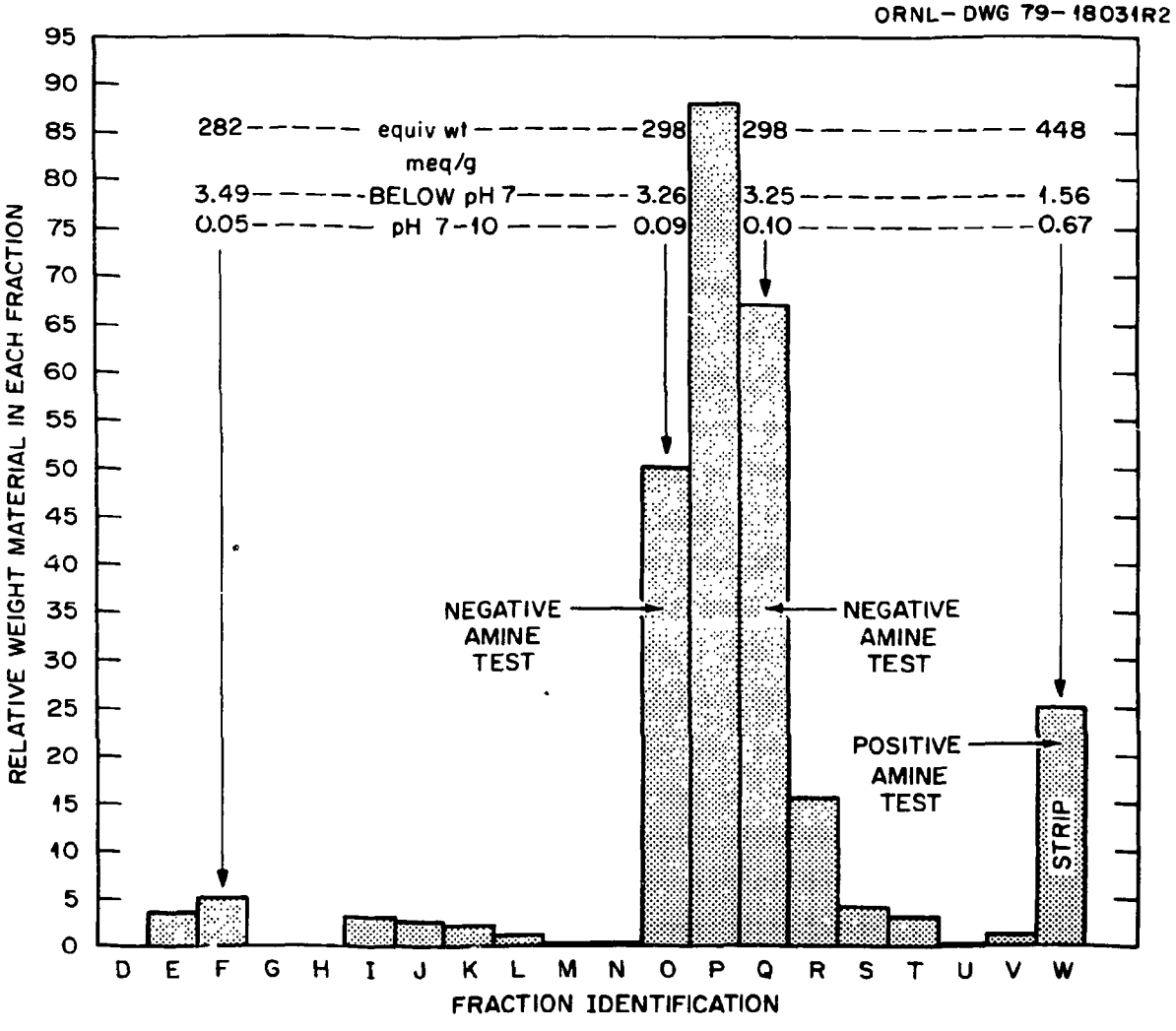



Fig. 2. Column chromatography of benzene extract of water solution obtained by acidification of the aqueous alkaline extract from the DHDECMP — diethylamine reaction mixture (sample 149).

irradiation is continued several hundred hours, the DHDECMP becomes a golden yellow, very viscous liquid that has a sharp unfamiliar odor and is slightly acidic. Significant amounts of NaOH or $HClO_4$ were required reach the end point of either an acid or base titration, indicating that the irradiated liquid was buffered. The observed rate of acid formation is 0.46 to 1.14 x $10^{-12}$ meq $rad^{-1}$ $g^{-1}$. The amounts of acid, amine and gas formed by radiolysis under various conditions are recorded in Table 5.

### 3.5 Removal of Radiolysis Products from DHDECMP without Alkaline Extraction

Purified DHDECMP that had been irradiated for 240 h (1.60 x $10^8$ rads $\cong$ 440 Wh $L^{-1}$) was found to contain 0.138 meq of acid per gram and to bind americium as shown in Table 2, entries 3 and 4. Passing 0.28 g of the irradiated substance in 10 mL of benzene through a column containing 2.5 g of Cellex-D ion exchange cellulose removed 90% of the americium-retaining radiolysis products (Table 2, entry 5). A 2.00-g sample was dissolved in 2% $CH_3OH$–98% $C_6H_6$ and fractionated in a Biosil-A column 21 cm long by 1 cm in diam. Fraction 103-I, 100 mL, contained 1.64 g of the oil; fraction 103-II, 50 mL, contained 0.133 g of oil; and fraction 103-III, 50 mL, eluted with up to 100% $CH_3OH$, contained 0.188 g of oil. This latter product (analysis: C, 55.37%; H, 10.02%; N, 4.31%), which had good binding power for $Eu^{3+}$, was fractionated further by column chromatography. The equivalent weights and amounts of acid for selected fractions are presented in Fig. 3. The EUAM data for this fraction are given in Table 2, entries 8 through 14.

Purified DHDECMP was irradiated to 3.08 x $10^8$ rads ($\cong$ 833 Wh $L^{-1}$) during a period of 21 d. The stripping characteristics of the irradiated material are recorded in Table 3, entry 2. Titration showed the presence of 0.226 meq of acid per gram. A 6.1-g sample of the irradiated DHDECMP was dissolved in 123 mL of benzene containing 2% $CH_3OH$ and fractionated through a Biosil-A column 1 cm in diam by 21 cm long. Fraction 115-I, 150 mL contained most of the DHDECMP but only 0.07 meq of acid per gram of DHDECMP. Fraction 115-II contained 0.19 g of oil in 20 mL of 4% $CH_3OH$–96% $C_6H_6$ and 0.79 meq of acid per gram of oil. Fraction 115-III contained

Table 5. Radiolysis of DHDECMP

| Irradiation time (h) | Wh $L^{-1}$[a] | Acid formed (equiv x $10^{-12}$ $rad^{-1}$ $g^{-1}$) | Amined formed (equiv x $10^{-12}$ $rad^{-1}$ $g^{-1}$) | Gas formed (mol x $10^{-12}$ $rad^{-1}$ $g^{-1}$) |
|---|---|---|---|---|
| 7 | 26 | 1.14 | | |
| 14 | 53 | 1.03 | | |
| 21[b] | 80 | 1.14 | | |
| 21[b] | 80 | 1.13 (1.26)[e] | | |
| 42 | 161 | 0.97 | | |
| 42 | 161 | 0.91 | | 0.7 |
| 42 | 161 | | | 0.7 |
| 94 | 361 | 1.11 (1.18)[e] | | |
| 185 | 712 | 0.66 | | |
| 185 | 712 | 0.65 | | 0.7 |
| 240 | 921 | 0.84 | 0.62 | |
| 240[c] | 921 | 0.74 (0.98)[e] | 0.65 (0.69)[e] | |
| 240 | 408 | 0.82 | | |
| 363[d] | 617 | | | 0.9 |
| 408[d] | 693 | 0.60 | | |
| 688[d] | 1180 | 0.85 | | |
| 498 | 836 | 0.66 | | |
| 883 | 3325 | 0.95 | 0.62 | |
| 1141[d] | 3800 | 0.56 | 0.45 | |
| 1331[d] | 4085 | 0.59 | | |
| 834 | 3895 | 0.46 | 0.36 | 0.71 |

[a] Assuming $10^8$ rads = 2.7 Wh $L^{-1}$.

[b] Sample saturated with water before irradiation, contained about 0.1 g $H_2O$/mL.

[c] Sample contained 5% $H_2O$ during irradiation.

[d] Calculations based on DHDECMP content of a 1 M DHDECMP in toluene.

[e] Values in parentheses are based on DHDECMP after correcting for mass of water present.

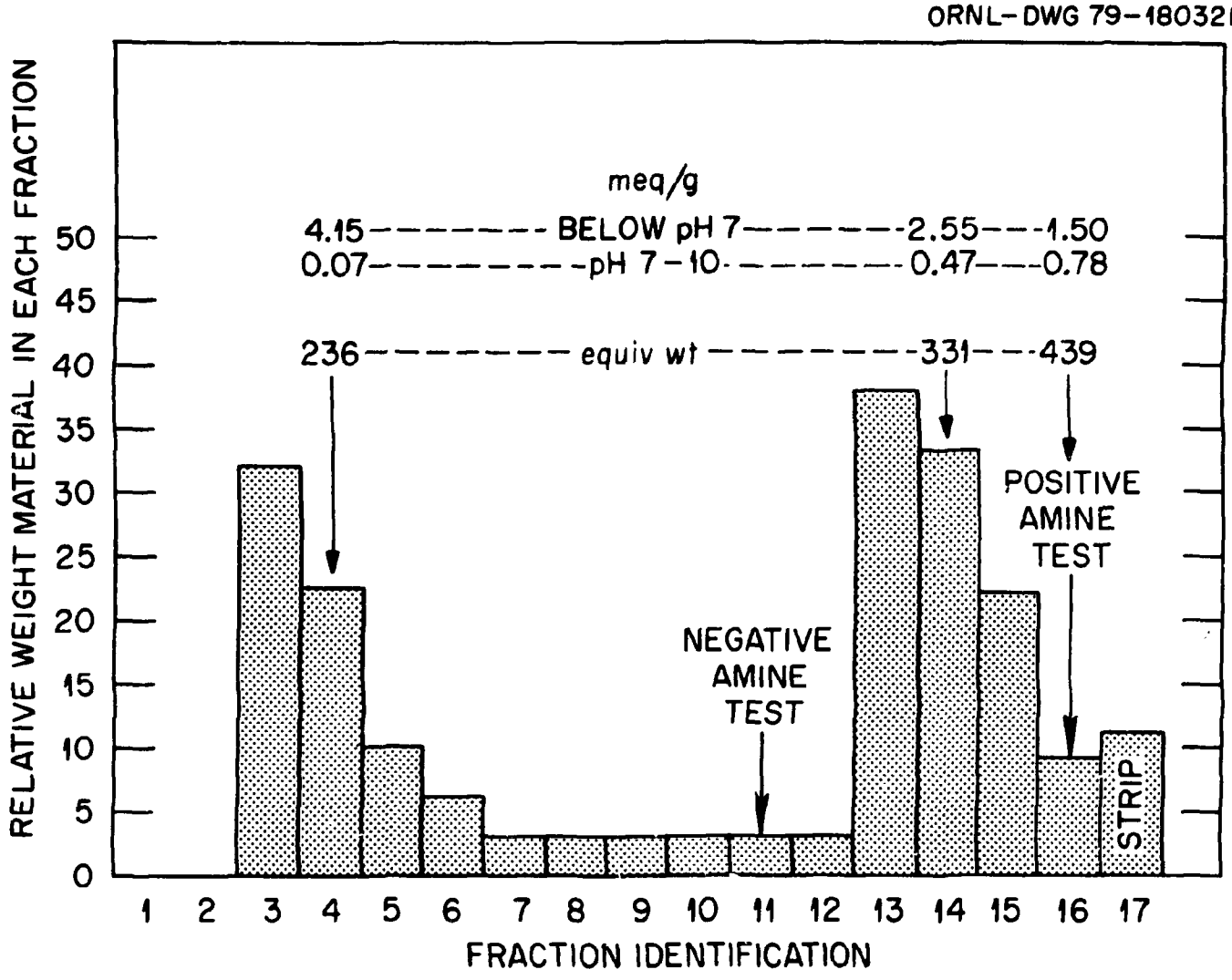



Fig. 3. Column chromatography of fraction 103-III obtained by the prior chromatography of irradiated DHDECMP ($1.60 \times 10^8$ rad). Only fractions containing significant amounts of solute are shown.

0.26 g of oil in 20 mL of 4 to 20% $CH_3OH$ in $C_6H_6$ and 1.5 meq of acid per gram of oil. Fraction 115-IV contained 0.16 g of oil in 20 mL of 20 to 100% $CH_3OH$ in $C_6H_6$ and 2.7 meq of acid per gram of oil. Fraction 115-V contained only 0.01 g of strongly acid oil in 20 mL of $CH_3OH$. Fraction 115-IV was refractionated by stepwise gradient elution using 2 to 100% $CH_3OH$ in $C_6H_6$ as shown in Fig. 4. It is reasonable to suppose that fractions F through H contained some neutral DHDECMP which reduced the number of milliequivalents of acid per gram. The relatively high nitrogen content of the fractions analyzed may be due to presence of amines, since no steps were taken to remove them.

### 3.6 Removal of Acidic Radiolysis Products from DHDECMP by Alkaline Extraction

A solution of 6.1 g of irradiated DHDECMP ($3.10 \times 10^8$ rads) in 60 mL of mixed hexanes was extracted consecutively with two 1.0-mL volumes of NaOH and washed with two 1.0-mL volumes of water. The aqueous volume after the first extraction was 2.7 mL, and the combined aqueous volume was 6.2 mL. The addition of 4.0 mL of $C_6H_6$ to the combined volume produced two layers, the lower containing 3.8 mL and the upper 6.0 mL. The aqueous layer was separated and washed twice with benzene, 3.0 mL and 2.0 mL, and then acidified by the addition of 2.00 mL of 1.00 N HCl. This formed a lower layer of oily product of about 0.3 to 0.4 mL and 5.1 mL of an upper layer. The acidic organic product that was recovered from the aqueous phase by extracting with two 2.0 mL portions of $C_6H_6$, evaporating the solvent, and drying at 0.13 Pa was a light yellow oil weighing 0.24 g (fraction No. 126-Pr). The combined benzene extracts from the alkaline solution spontaneously separated into 1.0 mL of lower, aqueous layer and 9.1 mL of upper layer. The upper layer was evaporated under reduced pressure to yield 0.98 g of pale yellow oil, fraction 127-B. The lower layer was acidified to liberate the organic acid which was recovered by extraction with benzene. Evaporation of the solvent yielded a yellow oil, fraction No. 127-A.

The fraction 126-Pr contained 3.4 meq per gram of acid which had an end point in ethanol which fell between that for dihexyl phosphoric acid (DHP) or HDECMP on one side and benzoic acid on the other. It also

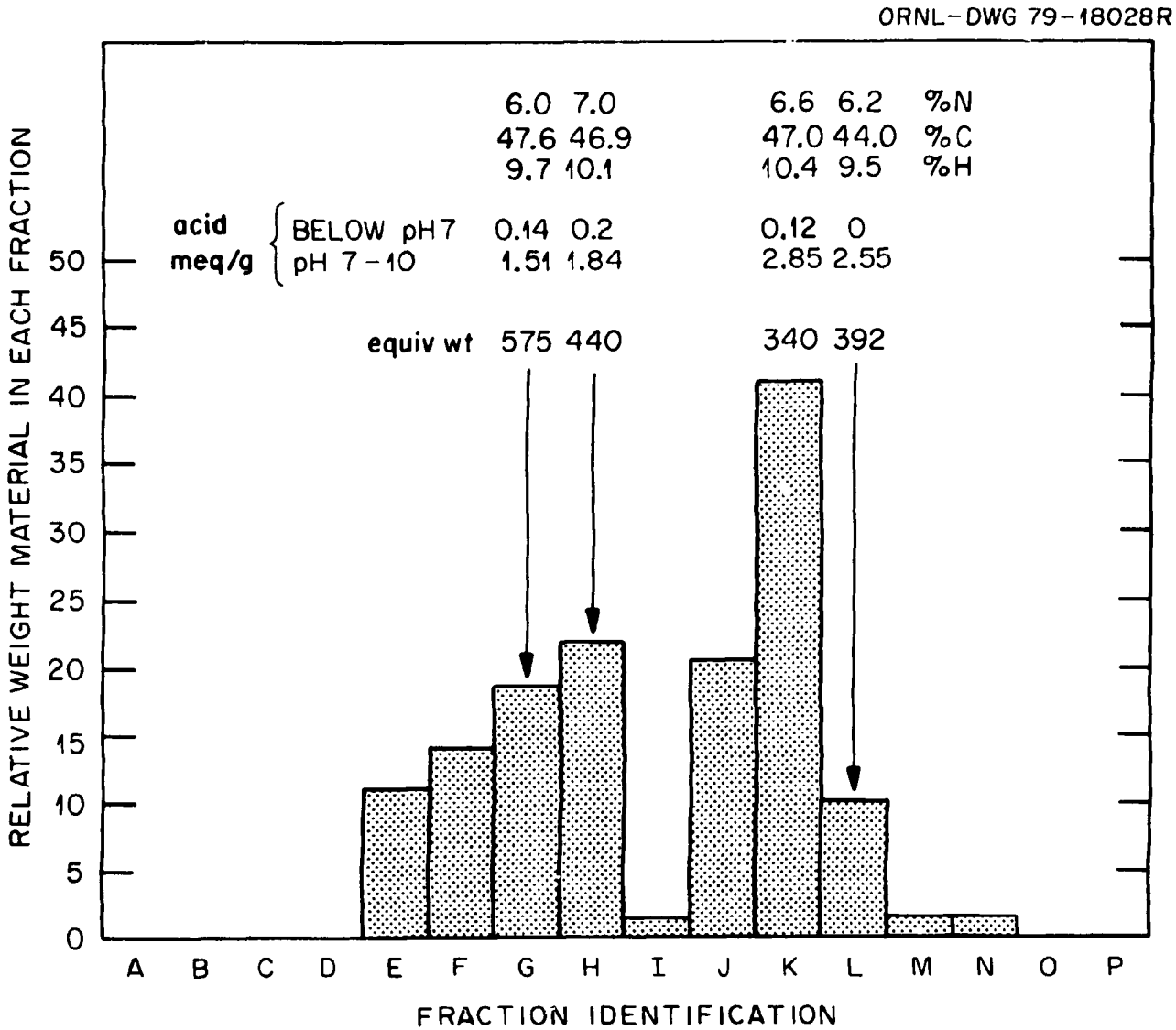



Fig. 4. Column chromatography of fraction 115-IV obtained by the prior chromatography of irradiated DHDECMP ($3.25 \times 10^8$ rads).

exhibited the ability to bind 0.43 mmol of $Eu^{3+}$ per gram in the EUAM test. The other two fractions contained less acid and had less binding power in the EUAM test, but the end point for the titration of fraction 127-A was at approximately the same point as for fraction 126-Pr. (It seems possible that the exposure to alkali during the slow separation process might have hydrolyzed an R-O-P linkage. Further data on fractions 126-Pr, 127-A, and 127-B are presented in Table 2, entries 15, 16, and 17.

Fraction 126-Pr was chromatographed by use of a Biosil-A column and stepwise gradient elution with 98% $C_6H_6$-2% $CH_3OH$ to 100% $CH_3OH$. The two largest fractions, 135-8 and 135-9, were combined and rechromatographed as shown in Fig. 5.

Fifty grams of irradiated DHDECMP [3.40 x $10^8$ rads (929 Wh $L^{-1}$)] which contained 0.213 meq of amine per gram and required the addition of 0.047 meq of NaOH per gram to reach "pH" 7 and 0.258 meq per gram to increase the "pH" from 7 to 11 was dissolved in 500 mL of mixed hexanes. After shaking this solution with 40 mL of 0.500 N NaOH, the phases separated into three clear layers. The volume of the middle layer, fraction No. 152-B, was 48 mL, but decreased to 35 mL after washing with two 50-mL and one 100-mL portions of hexane. The volume of the bottom layer, Fraction No. 152-C, was 16 mL. The two lower layers, 152-B and 152-C, were both evaporated in a rotary evaporator* and finally pumped down to less than 26.7 Pa (0.2 mm), in order to remove all volatile material, especially diethylamine. Each residue was acidified with a small excess of 1.0 N HCl and evaporated to dryness, and the organic material was extracted from the sodium chloride with benzene. The product 152-BP, 8.114 g after drying at 6.67 Pa (0.05 mm), required 0.169 meq of NaOH per gram to reach "pH" 7 and 0.405 meq per gram to increase the "pH" from 7 to 11. On the other hand, the product 152-CP, 0.414 g, required the addition of 2.47 meq of NaOH per gram to reach "pH" 7 and 0.44 meq of NaOH to raise the "pH" from 7 to 11.

A very small sample of 152-BP was put through a Waters** high performance liquid chromatographic C-18 column using gradient elution with

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*Büchi Rotavapor-RE, Brinkmann Instruments, Inc., Westbury, N.Y.

**Waters Associates, Inc., Milford, Mass.

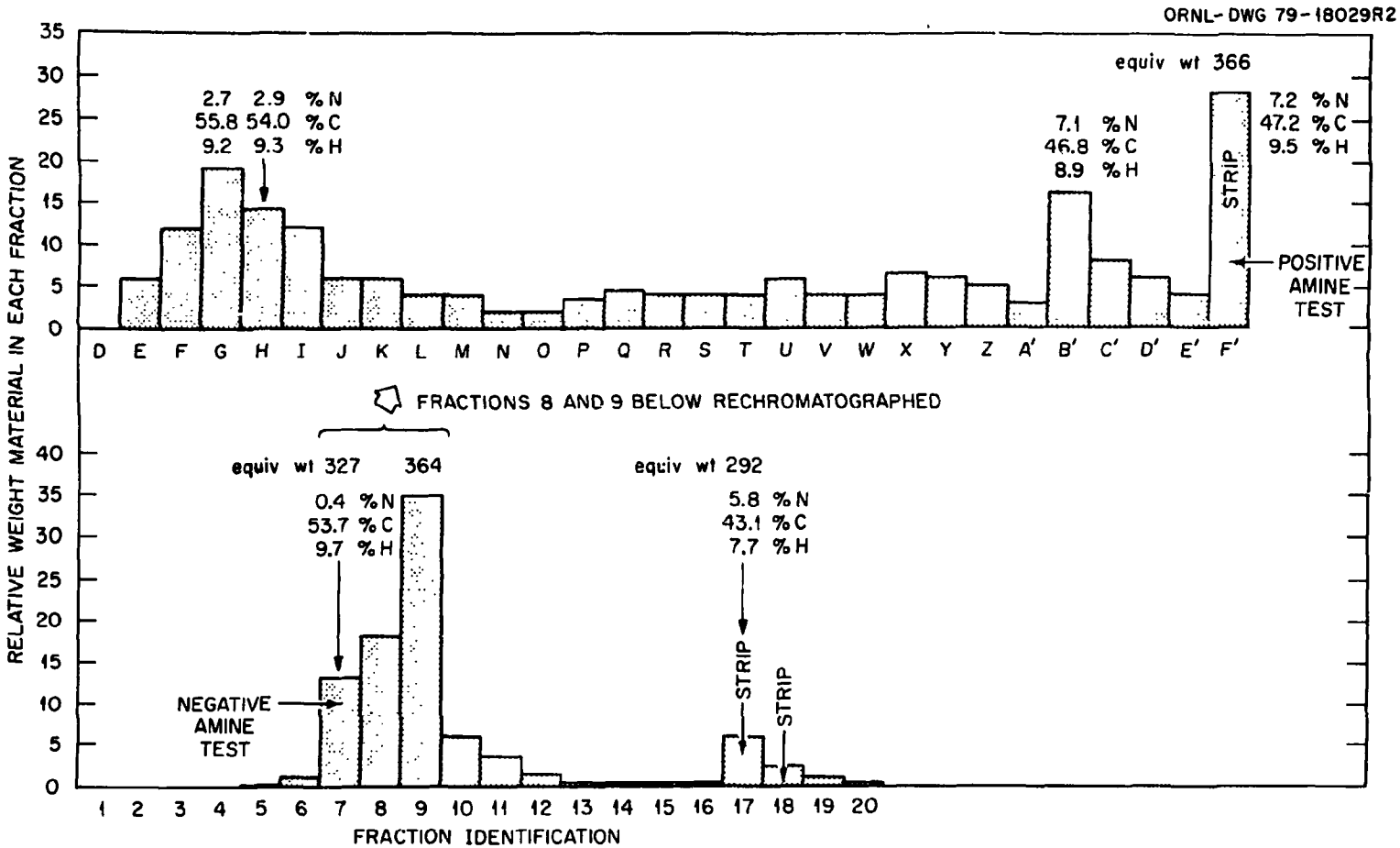


Fig. 5. Column chromatography of the combined fractions 135-8 and 135-9 resulting from the prior chromatography of fraction 126-Pr, a material recovered from irradiated DHDECMP ($3.1 \times 10^8$ rads) by aqueous alkaline extraction.

50 to 100% $CH_3OH$ and a 254-nm absorbance detector. This revealed the presence of more than 30 species, many of which appeared to be present in very small amounts. Absorbance at this wave length is not necessarily a good indication of the relative quantity of each substance.

A 1.1938-g portion of 152-BP was chromatographed by stepwise gradient elution with $C_6H_6$-$C_2H_5OH$ mixtures from a 32-cm BioSil-A column, and selected fractions were rechromatographed as shown in Fig. 6. Analyses of selected fractions are presented in Table 6.

### 3.7 Effect of Hydrogen Peroxide

Since various sources have suggested that radiation degradation is mainly the result of the attack of radiation-produced hydrogen peroxide, tests were made of the attack of hydrogen peroxide on DHDECMP. A mixture of 0.067 g of 30% $H_2O_2$ and 1.16 g of purified DHDECMP in contact for 7 and 17 d at room temperature produced 0.0048 and 0.0075 meq of acid per gram respectively. The titration curve was similar to that for irradiated DHDECMP.

## 4. DISCUSSION

### 4.1 Nature of Radiolytic Products

Preliminary studies of the gases liberated during irradiation have shown the presence of substantial quanties of hydrogen ($H_2$) and carbon monoxide (CO) along with smaller amounts of methane ($CH_4$) and various hydrocarbon fractions. This indicates a profound breakdown of the structure of the original molecule. A wide variety of products can result from the breaking of H-C or C-C bonds, including unsaturated compounds, compounds with shortened hydrocarbon chains, and those in which major groups have been removed. The presence of CO in the gaseous products of irradiation suggests that the $(C_2H_5)_2N$ portion of the amide has been split off; the presence of amines, as shown by titration, supports the view that attack on the amide portion of the molecule is important. Possible products are $(C_2H_5)_2NH$, $CH_3NHC_2H_5$, and $CH_3$-$CH{=}NC_2H_5$ and similar compounds. Pelah et al. have studied the mass spectrometry of N,N-diethyl-acetamide[17] and found that the loss of a terminal methyl from one of the ethyl groups occurs to

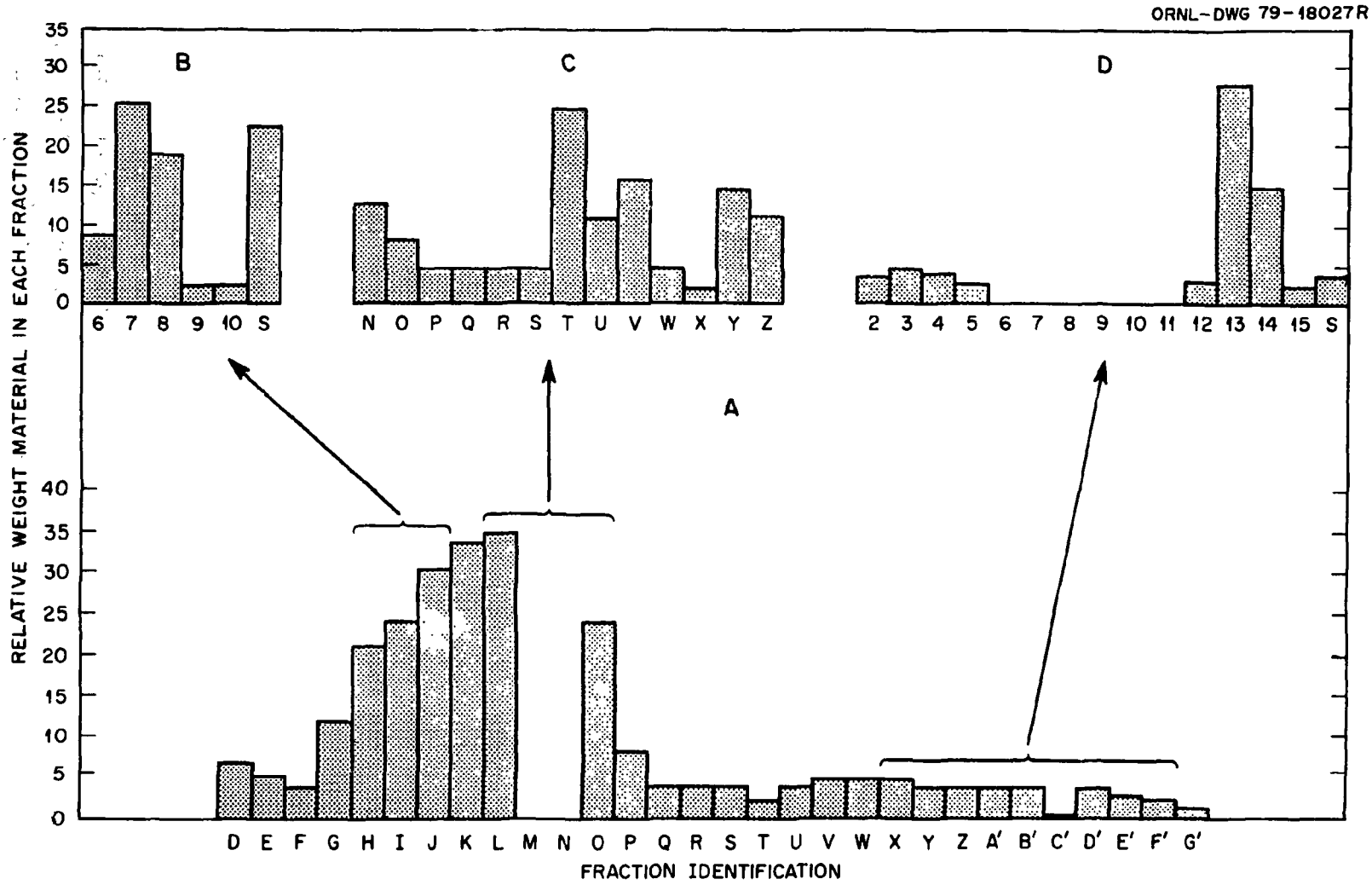


Fig. 6. Column chromatography of combined fractions obtained by the prior chromatography of fraction 152-BP, a material recovered from irradiated DHDECMP ($3.40 \times 10^8$ rads) by aqueous alkaline extraction.

Table 6. Analysis of selected fractions from Fig. 6

| Group | Fraction | % C | % H | % N | meq wt[a] |
|---|---|---|---|---|---|
| A | D | 56.0 | 11.1 | 0.1 | 318 |
| | F | 56.8 | 10.6 | 1.5 | 308 |
| | O | 56.0 | 10.2 | 3.8 | 267 |
| | U | 56.0 | 9.7 | 3.6 | |
| | W | 55.3 | 9.8 | 4.1 | |
| B | 6 | 56.5 | 10.4 | 0.9 | |
| | 7 | 57.9 | 10.7 | 1.7 | |
| | 8 | 57.9 | 10.5 | 2.4 | |
| | 10 | 53.3 | 10.2 | 2.9 | |
| C | N | 57.3 | 10.3 | 3.3 | |
| | S | 57.3 | 10.1 | 3.7 | |
| | T | 55.7 | 10.3 | 3.5 | |
| | V | 55.3 | 10.3 | 4.8 | |
| | W | 55.3 | 9.8 | 4.1 | |
| | Y | 53.6 | 10.2 | 4.4 | |
| | Z | 53.6 | 10.2 | 4.6 | |
| D | 3 | 60.3 | 9.6 | 4.8 | |
| | 14 | 51.9 | 9.9 | 5.1 | |
| | 15 | 50.0 | 9.4 | 5.9 | |

[a]Milliequivalent weight of fraction determined from weight and titration.

some extent, but the chief fragments observed are $CH_3-CH_2 \cdot HN^+=CH_2$ $HN^+C_2H_5$, and $CH_3{}^+CO$; their formation involves the breaking of the bond between the C=O and the N of the amide. They also present evidence for $[CH_3CONHCH_2CH_3]^+$ and $[CH_3CONH=CH_2]$.

Budzikiewica, Djerassi, and Williams[18] state regarding esters that "Saturated hydrocarbon ions corresponding to $R^+$ are formed by ejection of carbon monoxide from the $N-OCH_3$ species." By analogy we might have

$$(RO)_2P-CH_2\overset{\overset{O}{\|}}{C}-NR_2 \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}CH_2{}^+ + CO + \cdot NR_2.$$

In view of the many positions in which bonds may be broken by radiation, it is not surprising that many different compounds are formed as is evidenced by the results of high-pressure liquid chromatography of fraction 152-BP, the benzene extract of an aqueous-soluble product of the irradiation of DHDECMP. It would be very difficult to isolate any of these in pure form; nevertheless, chromatography on silica gel has provided useful information about the relative amounts and the types of groups of related compounds. The steps followed in preparing fraction 152-BP had removed most of the volatile amines, so that the first fractions to come off the column (Fig. 6) contained very small amounts of nitrogen; however, the nitrogen contents in the succeeding fractions increased (Table 6). Even though many compounds were involved, hydrogen contents close to 10% through a long series of fractions obtained from 152-BP indicate that the principal compounds present all contained about 10% H. Also many of the fractions had carbon contents of 55-57% regardless of their nitrogen contents (Table 6). It appears probable, then, that the first fractions, which had only a trace of nitrogen and were rather strongly acidic, included such substances as dihexylphosphonoacetic acid (C, 54.5; H, 9.5), dihexyl phosphate (C, 54.1; H, 9.8), and dihexyl phosphite (C, 57.6; H, 10.9). The nitrogen content of the middle fractions may be due to the presence of HDECMP (C, 51.6; H, 9.4; N, 5.0), DHDECMP (C, 59.5; H, 10.5; N, 3.85) and in some cases the diethylamine salt of dihexylphosphonoacetic acid (C, 56.9; H, 10.0; N, 3.7) or of one of the other acids mentioned above. The large milliequivalent weights found for some fractions suggest the presence of DHDECMP (or some other neutral compound) or of a high molecular weight amine.

In contrast to the preparation of fraction 152-BP where efforts were made to eliminate amines such as diethylamine, no special steps were taken to eliminate amines or DHDECMP in the preparation of fraction 115-IV (Fig. 4), so the fractions obtained from it by column chromatography probably consist largely of amine salts together with some DHDECMP in the earlier fractions.

It is interesting that the last fraction removed from the column by stripping nearly always gave a positive amine test even when the earlier fractions did not. This observation suggests that the presence of an

amine aids in binding the acidic radiolysis products to a silica column. It may be possible to take advantage of this fact in purifying DHDECMP.

The amines produced by radiolysis of DHDECMP have not yet been identified. Diethylamine is a probable product, but other amines are possible. Separation of the compounds by gas chromatography should not be too difficult. (In process use of DHDECMP for actinide extraction, the amines probably would go into the aqueous phase and might have some effect on the nitric acid solution.) Gas chromatographic separation of the components of both crude and purified DHDECMP has been done by McIsaac et al.[19]

### 4.2 Rates of Radiolysis

The rate of acid formation by radiation appears to decrease as the amount of radiation increases (Table 5). Possible explanations for this observation (assuming no systematic error in the method of analysis which leads to higher results for smaller quantities of acid) are (1) conversion of the primary acidic radiolytic product on further irradiation to yield less acidic secondary products, or (2) some catalytic effect which alters the course of chemical reaction. The latter explanation is favored by evidence (Table 5) suggesting that the rate of gas formation may increase with increasing radiation, but the data are inconclusive.

Other evidence suggests that water in the DHDECMP slightly increases the rate of acid formation per gram of anhydrous DHDECMP present, but the difference is not greater than the possible experimental error of measurement. The same comment applies to the use of toluene as solvent for the DHDECMP in comparison with irradiation of neat DHDECMP.

## 5. CONCLUSIONS

The formation of colored by-products when DEB is kept in contact with 6 or 4 N $HNO_3$ has been noted, but this does not seem to interfere seriously with the use of DEB as a diluent. The hydrolysis of DHDECMP by nitric acid presents a significant problem, especially at the higher acid concentrations. In addition to destruction of the extractant, HDECMP, an acid that prevents clean stripping of the extractant, is produced. While the problems

caused by HDECMP are known, the effect of another possible degradation product, dihexyl carboxymethylphosphonate, has not been examined. Use of 2 M $HNO_3$ appears to avoid most of the difficulty arising from acid hydrolysis.

While alkali does hydrolyze DHDECMP, the data presented indicate that the brief contact time in scrubbing processes for removing undesirable acids may do little harm.

The reaction of diethylamine with DHDECMP to form diethylhexylamine and HDECMP is slow, but it may have some use as a means of preparing HDECMP for further study, especially if DHDECMP becomes available at a lower price.

The observed rate of formation of acid products by radiolysis is not rapid enough to preclude use of DHDECMP as an extractant, but does require that some method for their removal be included in plans for its use. Adsorption on Bio-Sil A or Cellex-D, for example, or scrubbing by aqueous base have been found effective in removal of these acids.

Radiolysis gradually destroys DHDECMP and produces a large number of products; therefore, it is anticipated that, even though the most objectionable acids are removed efficiently, it will be necessary to replace the extractant eventually. The rate of radiolysis is not rapid, and the quantities of harmful products resulting from 2 to 20 Wh $L^{-1}$ of irradiation during five to ten weeks operation, as proposed by Schulz and McIsaac,[7] should be dealt with readily.

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