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BIDENTATE ORGANOPHOSPHORUS COMPOUNDS AS EXTRACTANTS*—I

EXTRACTION OF CERIUM, PROMETHIUM, AND AMERICIUM NITRATES

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Abstract—It is shown that tetraalkyl methylenediphosphonates $[(RO-)_2 P-CH_2-P(-OR)_2]$, di-O O $\| \|$ alkyl N,N-dialkylcarbamylphosphonates $[(RO-)_2 P-C-N(-R)_2]$, and dialkyl N,N-dialkylcarb-O O

amylmethylenephosphonates $[(RO-)_2 \stackrel{"}{P} - CH_2 - \stackrel{"}{C} - N(-R)_2]$ are powerful, chelating extractants for cerium, promethium, and americium from solutions of nitric acid.

TRIVALENT lanthanides and actinides are only poorly extracted from nitric acid solutions by monodentate compounds such as tri-n-butyl phosphate (TBP). Yet the highly acidic waste concentrates from such processes as the Purex process are important potential sources of radioisotopes of these elements. The poor extraction ability of the organophosphorus esters for these elements is due to back-salting by nitric acid that is extracted at the same time. One approach to improving extractant strength is to alter the molecular structure in a manner that will improve the extraction of these metals relative to that of acid.

The obvious approach to increasing the relative extraction of these metals is to employ bidentate extractants that are capable of chelation. Already BANKS *et al.*,⁽¹⁾ have

synthesized tetrahexylmethylenediphosphine oxide, $(C_6H_{13})_2P-CH_2-P(--C_6H_{13})_2$, and have shown that extraordinarily strong extraction of uranium (VI) is obtained with this compound. However, HEALY and KENNEDY⁽²⁾ were unable to observe an increase in the extraction of uranium (VI) by tetrabutyl methylenediphosphonate

(TBMDP), $(C_4H_9O_{--})_2P-CH_2-P(--OC_4H_9)_2$, as compared to extraction by analogous monofunctional compounds. Our preliminary investigations also failed to show any extraordinary extraction of uranium by TBMDP. However, poor material balance of

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⁽¹⁾ J. J. RICHARD, K. E. BURKE, J. W. O'LAUGHLIN and C. V. BANKS, J. Amer. Chem. Soc. 83, 1722-6 (1961).

⁽²⁾ T. V. HEALY and J. KENNEDY, J. Inorg. Nucl. Chem. 10, 128-36 (1959).

uranium was observed in this Laboratory which indicates that the TBMDP may not be completely soluble in benzene for the conditions in the test performed by HEALY and KENNEDY. In any event when tetrahexyl methylenediphosphonate was substituted for the butyl ester, uranium was extracted much more strongly than by monodentate analogues. This might be expected on the basis that the higher molecular weight of the hexyl ester would make it soluble in benzene even if the butyl ester were not. Further experiments with uranium extraction were postponed in favour of work with trivalent lanthanides and actinides. The purpose of this paper is to report the results of the earlier phases of this work. It is planned that this shall be the first of several papers concerning the behaviour of bidentate extractants. As such, it will be only in the nature of an introduction to the extraction of trivalent lanthanides and actinides. Later papers will cover details of mechanisms, a wider variety of organic structures, a wider range of extraction variables, and extraction of a diversity of elements.

PREPARATION OF MATERIALS AND EXPERIMENTAL PROCEDURES

O O = O O = 0The diphosphonates, carbamylphosphonates [(RO-)₂ P-C-N(-R)₂] and carbamylmethylene-O O O

phosphonates $[(RO-)_2 P-CH_2-C-N(-R)_2]$, used in this work were all prepared by the Arbuzov rearrangement. For example,

$$\begin{array}{c} & & & \\ \parallel & & \parallel \\ 2(C_4H_9O)_3P + CH_2Br_2 \rightarrow (C_4H_9O -)_2P - CH_2 - P(-OC_4H_9)_2 + 2C_4H_9Br. \end{array}$$

Yields of about 40 per cent of the second and third classes of compounds were readily obtained by O O O

rapidly adding the carbamyl chloride, $R_2 NCCl$, or chloroacetamide, $R_2 NCCH_2 Cl$, to an equimolar quantity of trialkyl phosphite that was already heated to about 200°C. The course of the reaction was followed by observing the distillation of by-product RCl. About 15 min was required to complete the reaction to the point where distillation had dropped to a very slow rate. At this point the reaction flask was removed from the heating bath in order to minimize the exposure of product to high temperatures.

The preparation of the diphosphonates, especially tetrabutyl methylenediphosphonate, is complicated by the fact that by-product alkyl halide cannot be removed with great rapidity from the reaction flask. (See article by CADE⁽³⁾ for a discussion of this problem). Since dibromides or diiodides must be used as starting materials, by-product bromides or iodides are formed and these are about as reactive as the starting dihalide. The result is a substantial loss of yield to the isomerization reaction,

$$\mathbf{RX} + (\mathbf{RO})_{3}\mathbf{P} \rightarrow (\mathbf{RO})_{2}\mathbf{RP} + \mathbf{RX}.$$

The best results were obtained in this Laboratory by the following procedure:

- (1) Add one-half mole of phosphite to one mole of alkyl dibromide at reflux and heat over night. The reaction flask is fitted with a fractionating column and the heating rate is set such that very slow distillation takes place.
- (2) The fractionating column is removed and the reaction flask is heated strongly to drive off excess alkyl dibromide and by-product alkyl bromide.
- (3) A further one-half mole of phosphite is added slowly with the heating bath at 180-200°C. After by-product distillation slows (total time about one hour), the reaction is considered complete.
- (3) J. A. CADE, J. Chem. Soc. 2266-72 (1959).

For the tetrabutyl ethylenediphosphonate and the propylene- and butylenediphosphonates, yields of 40 per cent can be obtained (based on phosphite). With TBMDP the fractionating column cannot be used effectively in step (1) since methylene dibromide and butyl bromide have nearly the same boiling point. Yields of TBMDP were 20–30 per cent. Dibutyl butylphosphonate was obtained from the Virginia-Carolina Chemical Co.

All extractants were distilled under high vacuum. After distillation, they were made up to 0.5 M in benzene and stirred with 6 M HCl at 60° C for 4 hr. The benzene solutions were then washed with water, a solution of sodium hydroxide, and twice more with water. Immediately after washing, the benzene was evaporated off and the extractants pumped down under high vacuum. This is essentially the procedure recommended by PEPPARD *et al.*⁽⁴⁾

In one trial the treatment with HCl was omitted with a sample of TBMDP. Extraction of cerium with this sample went through a minimum at about 0.1 M HNO₃ in the aqueous phase and then rose to high values at lower acidity. Evidently the treatment with HCl destroys some acidic impurity (or its parent compound) that would otherwise invalidate results obtained at low acidity. Such impurities would be expected because of the high temperatures required to synthesize and distill these compounds. As a further precaution the tracer solutions were made up to contain 0.003 M Ce(NO₃)₃ on the possibility that very low levels of impurities might be present and that they would be saturated by this concentration of cerium.

The failure to include the purification step with HCl, or a similar step, may account for the high extraction coefficients obtained by SAISHO⁽³⁾ with tetrabutyl ethylene-1,2-diphosphonate.

Equilibrations of 1 min duration were performed with a small electric stirrer. At three widely spaced points on the extraction curve, the attainment of equilibrium was tested by approaching equilibrium first with cerium initially in the aqueous phase and then repeated by having cerium initially in the organic phase. Satisfactory agreement (3 per cent mean deviation) was obtained in all cases except with dibutyl butylphosphonate and tetrabutyl butylene-1,4-diphosphonate. Above about 8.0 M nitric acid in the aqueous phase, both of these compounds gave some evidence of slow equilibria. This phenomenon was not investigated further, since neither of these compounds were of principal interest to the study. For this reason no data are reported for these two compounds at high HNO₃ concentrations in the aqueous phase.

²⁴³Am, ¹⁴⁴Ce, and ¹⁴⁷Pm were determined by conventional counting procedures. When the three elements were present in the same solution, ¹⁴⁴Ce and ¹⁴⁷Pm were determined by differential β -counting and ²¹¹Am bx α -counting. Small mounts (usually 25 *u*l) of the organic phase were made in order to minimize the problem of volatilizing these high boiling extractants and obtaining clean plates for α -counting. Even so, it was often necessary to prepare several plates in order that at least two could be obtained that were relatively clean. Mounts of the organic phase probably are the limiting source of error for the data for americium. A mean deviation of about 5 per cent in α -counting was obtained between duplicates. The extraction coefficients for cerium were generally determined with about 3 per cent mean deviation. The mean deviation for data with promethium was about 6 per cent, since they involved a determination by differences. However, as extraction coefficients approached 10², precision fell to about 10–15 per cent, and at 10³, precision was only within a factor of about two. This decrease in precision was apparently due to inability to obtain sufficiently complete separation of aqueous from organic phases even though the phases were centrifuged.

Water analyses were performed by the Karl Fischer method. Acidity was determined by ordinary acid-base titration. Densities were obtained by weighing 1-ml micropipettes filled with extractant.

RESULTS AND DISCUSSION

Data for the extraction of metals at 30° C are given in Figs. 1 and 2 and repeated in Table 1. Data for the extraction of nitric acid at 30° C are given in Table 2. Densities and the composition of the extractant phase at 23° C are given in Table 3 for all of the extractants. One set of data in Table 3 is given for organic samples that had been

⁽⁴⁾ D. F. PEPPARD, G. W. MASON and J. L. MAIER, J. Inorg. Nucl. Chem. 3, 215-28 (1956).

⁽⁵⁾ H. SAISHO, Bull. Chem. Soc. Japan 34, 859-61 and 1254-57 (1961).



FIG. 1.—Extraction of cerium at 30°C by various bidentates and by dibutyl butyphosphonate.

equilibrated with water; the other set is for samples that were in equilibrium with 6.5 M nitric acid. The data in all the tables and figures are for undiluted extractant.

The data of the first two tables and figures indicate that the bidentate extractants that can form five or six membered rings with Ce, Pm, and Am are chelating extractants. Extraction coefficients are approximately 100 times as large over most of the acidity range as those obtained with monodentates. However, in the diphosphonate series, extraction decreases sharply as additional bridging methylene groups are introduced between the phosphoryl groups.

It is true that both the propylene (TBPDP) and butylene (TBBDP) compounds are still slightly more powerful extractants than is dibutyl butylphosphonate (DBBP).



FIG. 2. -Extraction of cerium, promethium, and americium at 30°C by three bidentate extractants.

The order of extractant strength is TBBDP > TBPDP > DBBP. The greater extractant strength of the diphosphonates may be explained as due to the higher concentration of phosphoryl groups in these compounds. By that token one would expect the order to be TBPDP > TBBDP > DBBP. Possibly, in the TBBDP molecule, since the phosphoryl groups are farther apart, they have less of the effect of being electronegative substituents on each other. This may offset the slightly higher concentration of phosphoryl groups in TBPDP. However, even with the butylenediphosphonate, the two phosphoryl groups are not far enough apart to be completely

sphonate	coefficient	m Am) 240		78		20	3-8 7-8	3-0 3-7	.4 1.7		0-69 0-69)·28 0·24	shosphonate	Extraction	coemcient	Ce	0.35	0.78	1.08	1-12	1.21	0.73	0.36	0.211	0-060				
1 methylenedipho	Extraction	Ce	120 25(86	91 81	43	27 17	10.2	4.4	2.0	1.82) <i>LL</i> -0	0.29 (Dibutyl butyl	Nitric acid,	aqueous phase,	(W)	5.5	3-67	2.73	1-96	1.00	0-55	0.271	0.196	0.100				
Tetrabuty	Nitric acid, aqueous phase,	(W)	12.0	7-4	5.5	3-5	2.00	0-83	0-44	0-25	0.196	0.134	0-066	/lene-1,2- inate	Extraction	coefficient	Ce	3.3	3.3	3.8	4-7	6-2	7-1	7-2	7.3 -	6-2	4·2	2.36	1.32	1.10
ıylene-	ficient	Am	1000		68	19		1-7	0-53	0.18	0.125		0-069	etrabutyl ethy diphospho	ric acid,	ous phase,	(M)	2.2	8-4	8·3	6.7	5.4	5.0	3.88	3.11	2-62	1.65	0-85	0-49	0.405
amylmeth	ction coef	Pm	906		51	16		1·2	0:47	0.15	0.136		0-077	Ē	Nit	aquec		1												
V-diethylcarb phosphona	Extra	ల	440	260	48	17-6	8.2	1-85	0-72	0.26	0.180	0.059	0-058	ene-1,3- ite	Extraction	coefficient	ငိ	0-47	0-62	0.85	1.50	1.60	1.72	1.51	06-0	0-58	0.215			
Dibutyl N,	Nitric acid, aqueous phase,	(W)	12.0	10.3	8-7	7.2	6.0	4.48	3.14	1.98	1-47	0.78	0-70	Tetrabutyl propyl diphosphons	Vitric acid,	ueous phase,	(W)	11-9	8.3	6-7	5.0	4·11	2-98	1.76	0-83	0-431	0-196			
lonate	ficient	Am	48	76	118	161	66	32	10	4.6	2·8					aqı														
lyphosph	tion coeff	Pm	53	78	105	119	83	27	9.5	3.8	2.4			osphonat	raction	efficient	Ce	·12	.32	-01	9	99	99	-94	-55	-259	094			
ylcarbarr	Extrac	ဗီ	24-7	44	78	118	118	43	13-8	5.6	3.4	1-7		-1,4-diph	Ext	SOC		1	1	7	2	1	1	0	0	0	0			
Dibutyl N.N-dieth	Nitric acid,	(W)	11-6	10.5	0.6	7.3	4.74	2.60	1.28	0.65	0.38	0-20))	Tetrabutyl butylene	Nitric acid,	aqueous phase,	(W)	6.5	6.0	4.09	2.12	1-05	1.00	0-56	0.312	0.196	0.100			

888

Table 1.—Extraction of cerium, promethium and americium nitrates at 30° C, undiluted extractants

T. H. SIDDALL

Dibutyl N,N-di phosph	cthylcarbamyl- ionate	Dibutyl N,N-dia methylenepł	ethylcarbamyl- 10sphonate	Tetrabutyl diphosj	methylenc- ohonate	Tetrabutyl diphos	ethylenc-1,2- sphonate
Nitric ac	(M) bid	Nitrie ac	id (M)	Nitric a	cid (M)	Nitric	acid (M)
Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase
12.1	8·1	12.3	6.18	11-8	5.4	12.4	5.7
0.6	6.0	8.6	4.50	8.3	4·3	8.4	4.37
5.6	4·20	5-1	2.87	4.53	2.93	4.54	3.09
3.69	3-02	3.36	2-02	2.34	1.86	3.06	2.36
1.58	1.61	1.01	0.67	1.10	1.01	1.00	1.01
1.00	1.11	0-98	0.65	0.60	0.60	0.56	0-56
0-95	1-07	0.483	0.262	0.341	0.320	0·302	0.276
0.55	0.66	0.216	0.068	0.190	0.140	0.176	0.126
0.305	0-366	0-068	0.00	0.093	0-057	0.089	0.048
0.166	0.186						
0-098	0.100						
Tetrabutyl prop	ylene-1,3-diphosphc	nate	etrabutyl butylene-	1,4-diphosphonate		Dibutyl butylphc	osphonate
Ä	tric acid (M)		Nitric a	cid (M)		Nitric acid	(W)
Aqueous phase	Organic p	hase Ac	queous phase	Organic p	hase A	queous phase	Organic phase
12.3	5.9		12.3	5.9		12-4	5.1
8.5	4-47		8.5	4.34		8.3	3-69
4.80	3.28		4.60	3.20		4-22	2.77
3.24	2.50		3·00	2.40		2.94	2.28
1.17	1.21		1.21	1-32		1.19	1.24
1·01	1·07		1.00	1.14		1.01	1.11
0.54	0.63		0.57	0.70		0.60	0.71
0.298	0.331		0.329	0-392		0.355	0-396
0.178	0.169		0·206	0.219		0·214	0.188
0.106	0-080		0.129	0.114		0.120	0-075

Table 2.—Extraction of nitric acid at $30^\circ C$, undiluted extractants

Bidentate organophosphorus compounds as extractants—I

889

	NHO.	5 (M)	(M) O ₂ H		Mole	ratio
Compound	Aqueous	Organic	Organic	Density	HNO ₃ /Compound	H ₂ O/Compound
Tetrabutyl methylenediphosphonate	0	0	7.4	1.033		3.3
* •	6.5	3.76	2.9	1.111	1.84	1.4
Tetrabutyl ethylene-1,2-diphosphonate	0	0	8-3	1.025		3-9
	6.5	3-82	2.5	1.105	1.94	1.3
Tetrabutyl propylene-1,3-diphosphonate	0	0	10-1	1-023		5.1
4 e 64	6.5	3.79	2:5	1.106	1.97	1.3
Tetrabutyl butylene-1,4-diphosphonate	0	0	9.6	1.020		5-0
	6.5	3.81	2.6	1.101	2.07	1.4
Dibutyl N,N-diethylcarbamylphosphonate	0	0	3-4	1-020		1.1
	6.5	3.52	4·3	1.094	1.30	1.6
Dibutyl N.N-diethylcarbamylmethylenephosphonate	0	0	17-9	1.025		7.8
	6.5	4.59	5.8	1-132	1-90	2-4
Dibutyl butylphosphonate	0	0	4.6	0-952		1.4
	6.5	3-35	1-1	1-026	1-10	0.36

TABLE 3.—COMPOSITIONS OF VARIOUS ORGANIC PHASES

T. H. SIDDALL

independent of each other. As shown in Table 3, the ratio of moles of nitric acid extracted per mole of phosphoryl group is not as high as that obtained with dibutyl butylphosphonate. One explanation is that, even when separated by four methylene groups, phosphoryl groups still act as electronegative substituents on each other. Electronegative substituents are known to reduce extractant strength. The data for water extraction also show that the phosphoryl groups of the bidentate compounds do not act independently.

As far as can be deduced from the data in this paper, extraction by TBMDP and by dibutyl N,N-diethylcarbamylmethylenephosphonate (DBDECMP), aside from chelation, follows the same general type of mechanism as that encountered with ordinary organophosphorus esters. A neutral molecule of metal nitrate is complexed by extractant in the organic phase. Any decrease in slope of the extraction curves with increasing concentration of nitric acid can be interpreted as the result of increased back-salting as more nitric acid is extracted. The ratio of acid to metal extraction is greater for DBDECMP than it is for TBMDP. As a consequence, the extraction curve for the metals with DBDECMP actually passes through a maximum while the slopes with TBMDP decrease only moderately, if at all.

On the other hand, it would be hard to say that extraction with dibutyl N,Ndiethylcarbamylphosphonate (DBDECP) follows this same general mechanism. Extraction with DBDECP shows an exponential rise with increasing acidity. In fact a good straight line is obtained when extraction coefficients are plotted against aqueous acidity on semilog paper. Back-salting by nitric acid is offset by some new factor. A simple explanation is that metal extraction by the carbamylphosphonate is based on an anion mechanism,

$$M^{3+}$$
 + $(3 + x)NO_3^-$ + xH^+ + $y(DBDECP) \Rightarrow H_xM(NO_3)_{3+x}(DBDECP)_y$

Further experiments now in progress and to be reported in a later paper indicate that the choice of a mechanism of this type is correct.

The data of Fig. 2 indicate that there is a tendency for the relative order of extraction of metals to change as the concentration of nitric acid changes. At low concentrations the order is $Ce > Am \simeq Pm$, but at high concentrations the order is $Am \simeq Pm$ > Ce. The effect is small and no explanation is obvious.

The question arises as to what other electron-donating groups might serve as the functional groups in chelating bidentates for the extraction of trivalent lanthanides and actinides. Preliminary experiments in this Laboratory show that strong extractants can be obtained by including a carbonyl group and a phosphoryl group in the same molecule. Unfortunately pure samples of carbonylphosphonates were not obtained in the synthesis of these compounds. The Perkow Reaction appears to be a competitive reaction with the Arbuzov rearrangement, which leads to a difficult problem in purification. Further investigations of the synthesis are planned.

Diamides do not seem to be chelating extractants for these trivalent lanthanides and

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actinides. Both tetrabutyl oxalamide, $(C_4H_9-)_2N-C-C-N(-C_4H_9)_2$, and tetra-OOO butyl malonamide, $(C_4H_9-)_2N-C-CH_2-C-N(C_4H_9)_2$, gave very low extraction

10

coefficients for cerium from 12 M HNO_8 . Chemical analysis, proton magnetic resonance spectra and infra-red spectra indicated that a fairly pure sample of the oxalamide was obtained; however, the malonamide contained some unidentified impurity. The failure of these diamides to act as chelating extractants is rather surprising in view of the effectiveness of the amide group in the carbamylphosphonates and carbamylmethylenephosphonates. No explanation is readily apparent for this behaviour.

In conclusion it is seen that very powerful bidentate extractants can be obtained for the trivalent lanthanides and actinides. These extractants or their homologues promise to have practical utility for the recovery of these elements from a variety of sources such as the high activity waste of the Purex process. The extractants whose behaviour is reported in this paper probably have about as low a molecular weight as can be useful; tetraethyl methylenediphosphonate, for example, is water soluble. Even larger molecules than those studied here may be desirable. Tetrabutyl methylenediphosphonate is limited in usefulness as an extractant when diluted with ndodecane because the dilutions form two organic phases when contacted with a variety of aqueous phases. Higher homologues such as the tetraamyl and tetrahexyl esters may be diluted without encountering serious problems from the formation of two organic phases. The higher homologues are easily synthesized, but their purification is complicated by progressively higher boiling points.