Steric Aspects of Selectivity of Organophosphorus Extractants

M. I. Kabachnik

A. N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of USSR, 117813, Moscow, Vavilov Str., 28, USSR.

ABSTRACT

This paper is devoted to the steric aspects of the efficiency and selectivity of extractants in the process of extraction of metal cations from acidic aqueous solution into a nonpolar phase. The extraction of uranium, plutonium, americium, and europium by tertiary carbamoylmethyl phosphine oxides and polydiphenylphosphinylmethyl benzenes have been studied. The separation factors of uranium and plutonium from americium are measured. Tertiary carbamoylmethyl phosphine oxides and diphenylphosphinylmethyl benzenes of the ortho type are characterized by unusually high separation factors. The diphenylphosphinylmethyl derivatives of benzene of the meta type do not possess a high selectivity in the process of separation of uranium and plutonium from americium, but are more efficient in extraction of americium.

The results of some of our studies on organophosphorus complexones were reported at the International Conference on Phosphorus Chemistry held in Tallin a year ago. The attention of the audience was drawn to the problems of efficiency, especially selectivity of binding metal cations to complexes. The subject matter of the lecture was the important role played by complementary geometries of the complexing ligand and the metal coordination.

This paper is in essence a continuation of the previous one. Our topic will be neutral complexing agents with phosphoryl groups, which recently have acquired great importance as extractants that transfer metal cations from an aqueous solution into a nonpolar phase. It should be borne in mind that the process of extracting metal cations by neutral organophosphorus extractants is a fairly complex one. It has received a sizable special literature, which includes studies concerned with the topic of this lecture, the problem of dependence of the efficiency and selectivity of extractants on their structure. Attention has mainly been given to the influence of substituents at phosphorus on the basicity and nucleophilic properties of phosphoryl groups responsible for the formation of complexes and therefore extraction [1, 2]. Less attention has been paid to problems of steric interactions.

As is known, an equilibrium describing the extraction of metal salts from strongly acidic aqueous media to a nonpolar phase can, in a most primitive way, be represented by Scheme 1:

SCHEME 1

1042-7163/91/$3.50 + .25   1
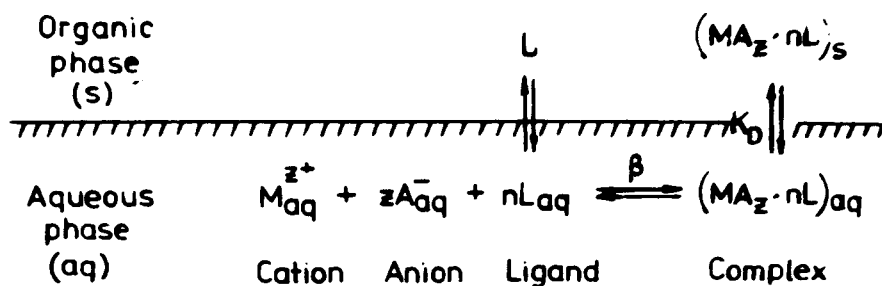
According to this scheme, the chemistry of the aqueous phase involves the formation of complexes with the stability constant given by the concentration Equation (1):

$$\beta = \frac{[MA_z \cdot nL]_{aq}}{[MA_z]_{aq}[L]^n_{aq}} \; ; \qquad (1)$$

$$K_D = \frac{[MA_z \cdot nL]_s}{[MA_z \cdot nL]_{aq}} \; ; \qquad (2)$$

The resulting complex is extracted from water into the nonpolar phase to the extent determined by the distribution coefficient K_D (Equation 2). In extraction experiments, the coefficient of the distribution of a metal between two phases, D, is usually determined. The value of D is given by Equation (3):

$$D = \frac{[MA_z \cdot nL]_s}{\sum\limits_{z=0} \sum\limits_{n=0} [MA_z \cdot nL]_{aq}}$$

$$\cong \frac{[MA_z \cdot nL]_s}{[M]_{aq}} \; ; \qquad (3)$$

With radioactive metals, the layers are separated after the attainment of equilibrium, and the activities of separate phases are measured. The quantity D is obtained as their ratio. Clearly, this quantity is not an equilibrium constant; nevertheless, it gives a fairly good estimate of the extractant's extraction ability. It is related to the stability constant of the complex β through Equation (4) [3].

$$\beta = \frac{D}{K_D[L]^n} \; ; \qquad (4)$$

$$\overline{K} = \frac{[MA_z \cdot nL]_s}{\gamma_\pm [M^{z+}]_{aq} ([L_0] - n[MA_z \cdot nL]_s)^n} \qquad (5)$$

Instead of D, the effective extraction coefficient $\overline{K}$ [4] is often used (Equation 5). It describes the partial equilibrium (Equation 6):

$$M^{z+}_{aq} + zA^-_{aq} + nL \overset{\overline{K}}{\rightleftharpoons} [MA_z \cdot nL]_s \qquad (6)$$
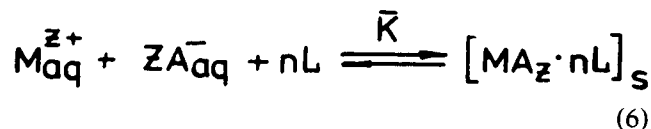
Of course, Equations (1) to (6) are only very approximate ones. They disregard many important factors influencing the extraction process, such as the distribution of acid and water between the two phases, a step-wise nature of the formation of complexes, a nonideal nature of solutions, and many others. It is essential that these equations clarify the physical sense made by the quantities used below.

In the 1970s, we had been investigating the problem of polar effects on the formation of complexes and extraction. Objects studied were diphosphine dioxides of the general formula (A):

(A)

(B)
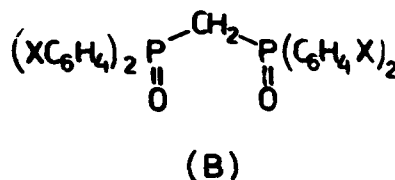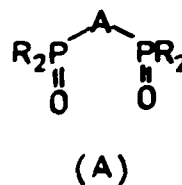
In particular, diphosphine dioxides (B) were tested. The dependence on the substituent X of the effective coefficient of extracting uranium from nitric acid into chloroform was determined [5]. The K values varied over a wide range. Electron donors X increased the effective extraction coefficient. A linear correlation with the $\Sigma\,\sigma^\varphi$ constants was observed: $\log K = -0.06 - 4.435\,\sigma;\ r = 0.968,\ s = 0.85,\ s_p = 0.30;\ n = 11$ (Figure 1). The stability constants of the complexes formed by these ligands, with copper chloride in acetone, vary similarly [6]. Here again a linear correlation with the constants σ^φ was observed, although the slope is far less steep: $\log K = 3.70 - 0.284\,\sigma^\varphi;\ r = 0.967,\ s = 0.08,\ s_p = 0.03;\ n = 9$ (Figure 2). We carried out a rather extensive study of alkylenediphosphine dioxides as extractants and found them to be very efficient although only moderately selective [7]. The ligands studied are illustrated in Scheme 2. The ability of the extractants to transfer uranyl from nitric acid solutions to chloroform decreased along a series [8]: R = Ph; (IV) > (VII) > (I) > (II) > (III) > (VIII) > (VI) > (IX). The most active species were the dioxide with the cis-vinylene bridge (IV) and its adduct with cyclopentadiene (VII). The trans-structured and acetylene-bridged dioxides were the least effective compounds in the series; they acted as unidentate ligands.

The bidentate ligands studied, especially diphosphine dioxide with the cis-vinylene bridge, were found to be high-efficiency extractants for uranium,
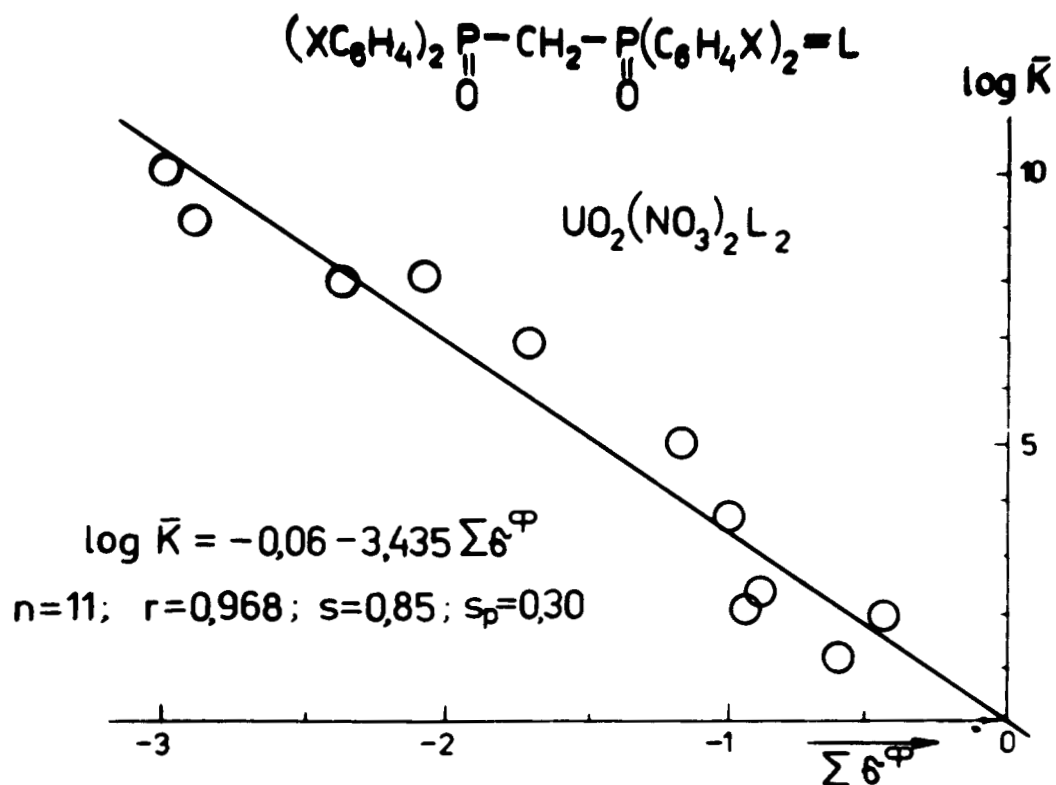
$$(XC_6H_4)_2 \underset{O}{\overset{\parallel}{P}} - CH_2 - \underset{O}{\overset{\parallel}{P}}(C_6H_4X)_2 = L$$

$\log \bar{K}$

$UO_2(NO_3)_2 L_2$

$$\log \bar{K} = -0.06 - 3.435 \, \Sigma \delta^\varphi$$

$$n=11; \quad r=0.968; \quad s=0.85; \quad s_p=0.30$$

$\Sigma \delta^\varphi$

FIGURE 1 Correlation of the effective extraction coefficient K and $\Sigma \delta^\varphi$ constants for extraction of U^{VI} by $(XC_6H_4)_2P(O)CH_2P(O)(C_6H_4X)_2$ from HNO_3 into $CHCl_3$.

$$(XC_6H_4)_2 \underset{O}{\overset{\parallel}{P}} - CH_2 - \underset{O}{\overset{\parallel}{P}}(C_6H_4X)_2 = L$$

$\log \beta$

$$(CuClL)^+ Cl^-$$

$$\log \beta = 3.70 - 0.284 \, \Sigma \delta^\varphi$$

$$n=9; \quad r=0.967; \quad s=0.08; \quad s_p=0.03$$

$\Sigma \delta^\varphi$
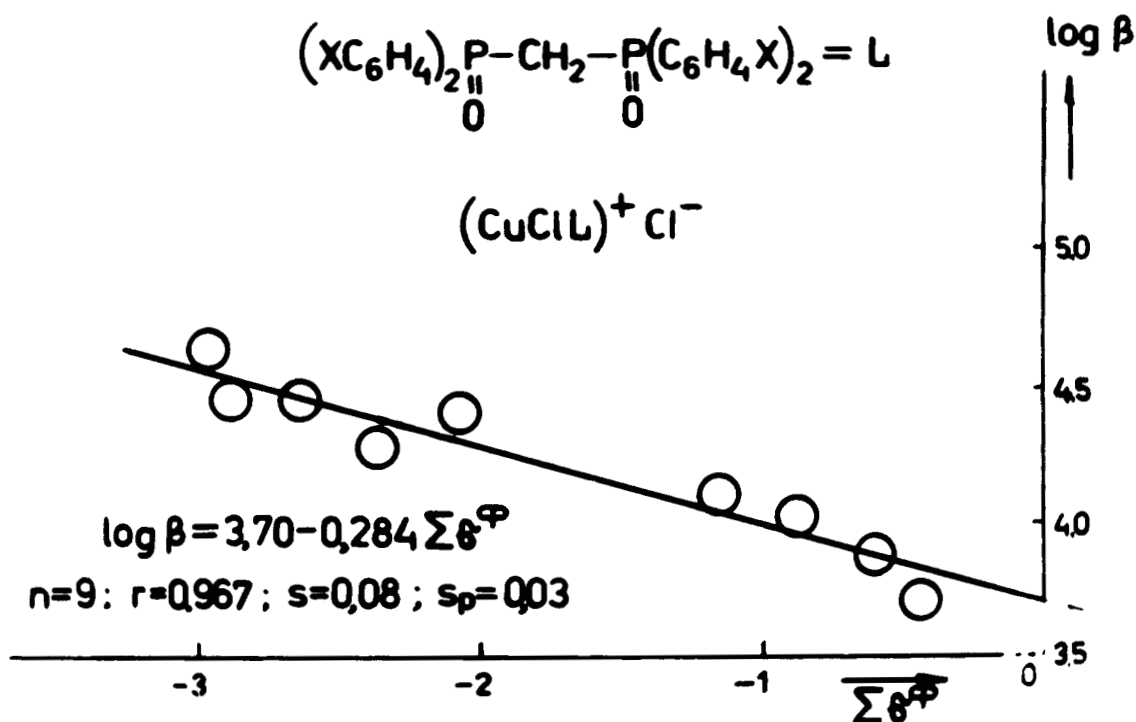
FIGURE 2 Correlation of stability constants, β, and $\Sigma \delta^\varphi$ constants of $CuCl_2$ complexes with $(XC_6H_4)_2P(O)CH_2P(O)(C_6H_4X)_2$ in acetone.
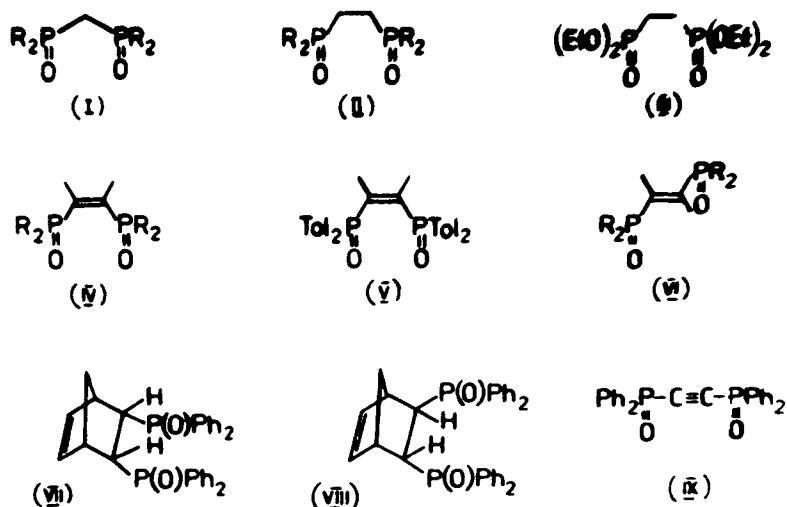
SCHEME 2

plutonium and trans-plutonium elements [9]. The following series should be mentioned:

$$Pu^{IV} > U^{VI} > Pa^{V} > Am^{III}$$
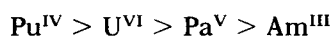
Also consider the following series [10, 11]:
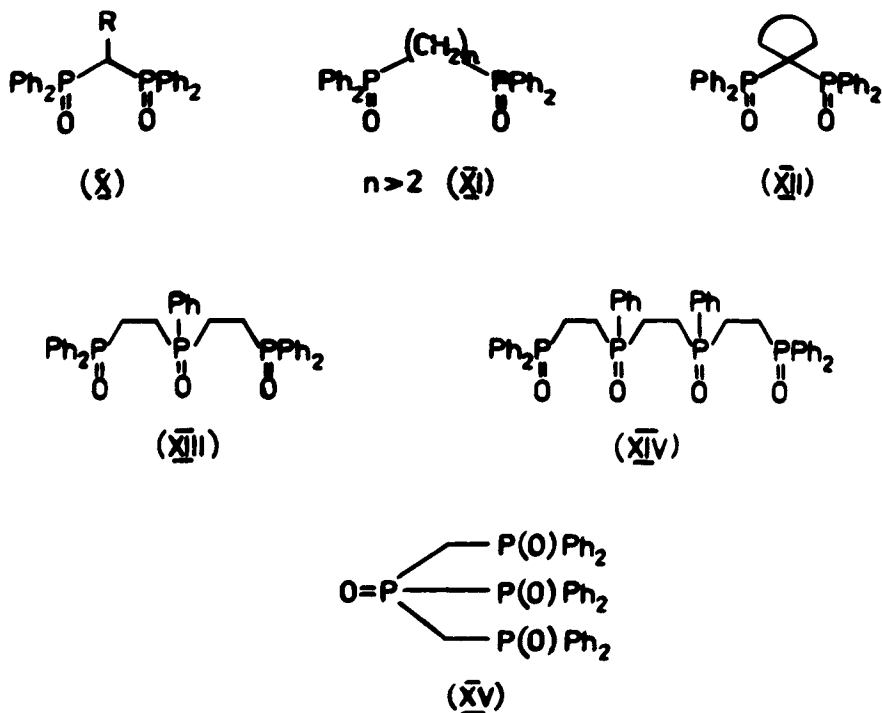
$$Bk > Cf > Eu > Am > Cm$$

Note that europium stands in the middle of the series, which is indicative of the absence of extraction selectivity between transplutonium and rare-earth elements. All the compounds studied except for those that behave like unidentate ligands (that is (VI), (VIII), and (IX)) are very efficient but rather unselective extractants.

Similar results with only minor variations were obtained for the phosphine di- and polyoxides found in Scheme 3 [12].

Our understanding of all these observations is based on the following ideas. Stability of coordination compounds extracted into a nonpolar medium depends first of all on the strength of bonds between ligand donor centers and the metal and
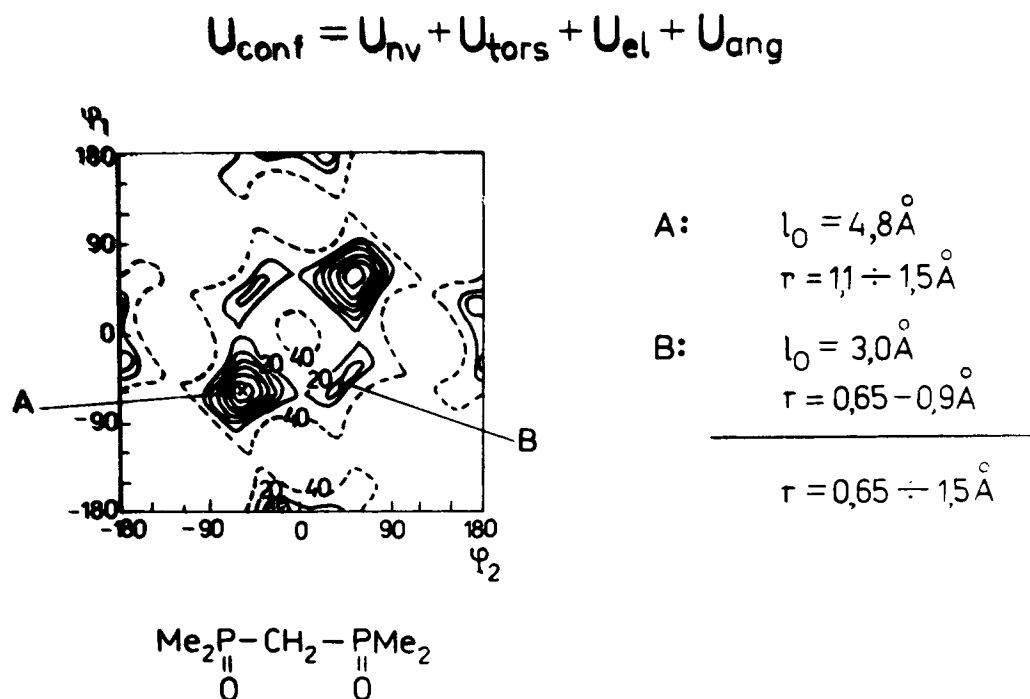

SCHEME 3

$$U_{conf} = U_{nv} + U_{tors} + U_{el} + U_{ang}$$

A: $l_0 = 4{,}8 \overset{\circ}{A}$

$r = 1{,}1 \div 1{,}5 \overset{\circ}{A}$

B: $l_0 = 3{,}0 \overset{\circ}{A}$

$r = 0{,}65 - 0{,}9 \overset{\circ}{A}$

$r = 0{,}65 \div 1{,}5 \overset{\circ}{A}$

$$Me_2\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{P}}} - CH_2 - \overset{\|}{P} Me_2$$

FIGURE 3 Conformation energy map for $Me_2P(O)CH_2P(O)Me_2$. Energy is given as a function of the rotation angles, φ_1 and φ_2 of CH_2—P bonds. Numbers are energy levels in kJ/mol.

the number and character of chelate rings. These relationships have been studied fairly well. There is, however, one more factor whose action is especially pronounced when the first two are not varied. This is the geometrical correspondence of the ligand conformation to the metal coordination polyhedron. Ligands with flexible atomic chains between ligand donor centers can always assume an energetically favorable conformation that meets the steric requirements of the cation. Therefore, these ligands should show only low selectivities. Conversely, the introduction of rigid fragments between donor groups should increase selectivity, other conditions being equal.

Molecular mechanics techniques were used to estimate conformational energies and geometries of conformations participating in the formation of complexes.

For simple systems, the conformational energy was calculated according to the usual additive scheme:

$$U_{conf} = U_{nb} + U_{tors} + U_{el} + U_{ang} \qquad (7)$$

where U_{nb}, U_{tors}, and U_{el} are the energies of nonbonded, torsion, and electrostatic interactions, respectively, and U_{ang} is the angle strain energy. The U_{conf} quantity was varied over all independent conformational transition parameters to determine the characteristics of stable conformers. These data were used to construct conformational energy maps. An example is given in Figure 3 in which the conformational energy map for the tetramethylmethyle-

nediphosphine dioxide, $Me_2P(O)CH_2P(O)Me_2$, is depicted [13]. The map is indicative of the presence of a global minimum A and a local one, B. Conformer A has a shallow minimum with the oxygen-oxygen spacing of $l_o = 4.8$ Å. It can therefore form complexes with large cations of 1.1 to 1.5 Å radii. In conformer B, the minimum is also shallow and the spacing is $l_o = 3$ Å, which makes it suitable for the formation of complexes with cations of 0.65 to 0.9 Å radii. A special calculation was performed to show that the substitution of four phenyl groups for methyl groups did not affect the positions of the minima. It follows that methylene diphosphine dioxides in stable conformations (differing in energy by 2–3 kcal/mol) are capable of meeting steric requirements of many cations with ionic radii of 0.65 to 1.5 Å. According to calculations, diphosphine dioxide with the cis-vinylene bridge (IV) should show a high selectivity. It should preferably combine with cations of ionic radii not exceeding 0.88 Å [14]. These are, of course, only very approximate conclusions, for solvation can affect the energy characteristics and the shape of conformers. In addition, the steric bonding conditions are determined, on the part of cations, by the size and shape of the coordination polyhedra and the lengths of actually formed coordination bonds rather than mean ionic radii. Nevertheless, these conclusions make up a reasonable basis for comparisons. Table 1 contains stability constants of alkali metal complexes with the dioxides under consideration. The corresponding coordination bonds are of essentially

TABLE 1 Stability Constants of Alkali Metal Complexes with Ligands L = $Ph_2P(O)$—A—$P(O)Ph_2$; Equilibrium CH_3COOM + L==ML^+ + CH_3COO^-; EtOH + $CHCl_3$

	M^+		Li^+	Na^+	K^+	Cs^+	$log\ K_{Li}$ –
A		r, A	0.68	0.97	1.33	1.67	$log\ K_{Cs}$
cis —CH=CH—		(IV)	2.52	2.08	1.65	1.43	1.09
—CH_2—		(I)	1.71	1.62	1.35	1.19	0.52
—CH_2CH_2—		(II)	1.05	0.89	0.78	0.84	0.21

ionic nature, which place the steric conditions of bonding above other factors [15]. One can see that the vinylene-bridged dioxide is the most selective ligand. The selectivity series is (IV) > (I) > (II), in agreement with the calculated results. Note that the same ordering, (IV) > (I) > (II), was observed in extracting uranium from nitric acid into chloroform.

One more object of our studies was carbamoyl derivatives of phosphine oxides of the general type (C).

(C)
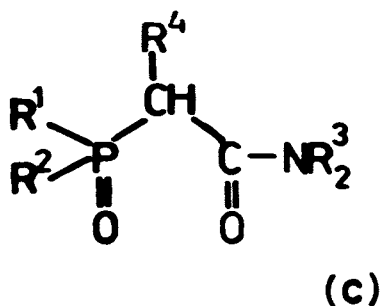
Ligands of this group differ from those discussed previously by the presence of the carbamoylmethyl group instead of one of the phosphoryl functions. This difference lowers compound basicities substantially, as can be seen from a comparison of their pK_a values determined in nitromethane [16, 17]:

Compound	$R_2P(O)CH_2P(O)R_2$	$R_2P(O)CH_2CONEt_2$
R = Ph	pK_a = 6.24	pK_a = 4.3
R = Bu	pK_a = 8.22	pK_a = 5.7

At the same time, molecular mechanics calculations are indicative of a high similarity of conformational transitions in the two compounds (R = Ph). Both form three stable conformations with l_o = 6.5, 4.6, and 3.0 Å (dioxide) and l_o = 5.5, 4.5, and 3.0 Å (carbamoylmethyl oxide) [18]. The l_o = 3.0 Å conformations can only participate in the formation of complexes.

When undertaking a study of this group of compounds, we understood perfectly well that, so far as extraction efficiency is concerned, it should be inferior to the preceding one; however, we expected it to show a higher selectivity.

It should be noticed that, at the start of this study, the corresponding phosphonates (RO) $_2P(O)$—

$CH_2C(O)NR_2$, were known and suggested as extractants for transplutonium elements [20].

Even our first studies of the extraction properties of tertiary carbamoylmethyl phosphine oxides revealed their high extraction ability towards actinides and showed them to form bidentate complexes [21]. According to expectations, they proved to be weaker but more selective extractants than tertiary alkylene diphosphine dioxides.

Ligands of general type (C) mentioned above were also studied [22]. Substituents at phosphorus, nitrogen, and the central carbon atom were varied. Actinides were extracted from nitric acid into dichloroethane by the extractant in concentrations of 0.05 to 0.1 M. The distribution coefficients (log D) were studied as depending on nitric acid concentration (0.01 to 10 M). The extracted cations were $^{241}Am^{III}$, $^{152-154}Eu^{III}$, $^{233}U^{VI}$, and $^{239}Pu^{IV}$. An example is given in Figure 4. One can see that, for plutonium, log D is larger than it is for uranium, while for americium, it is lower than for both plutonium and uranium. It should be noted that, for americium (as for transplutonium elements in general), the log D values are fairly high.

Especially attractive is the high selectivity observed in extraction of these three elements. In Table 2, the separation factors for uranium/americium and plutonium/americium are given and compared with that for americium/europium. The factors for the separation of uranium and plutonium from americium are unusually high. So far as the separation of americium and europium (that is, transplutonium elements/rare earth elements) is concerned, the corresponding factors do not exceed two. These findings characterize tertiary carbamoylmethyl phosphine oxides as extractants for extracting transplutonium elements together with rare earth ones. These phosphine oxides are exceedingly interesting substances in this respect.

A comparison of selectivity characteristics of this group of extractants and the most selective ligand among the preceding group of diphosphine dioxides, tetraphenyl cis-vinylene diphosphine dioxide (IV), (Table 3) shows carbamoylmethyl derivatives to be far superior.

It should however be noted that the group of tertiary carbamoylmethyl phosphine oxides is not characterized by the ability to separate transplutonium elements from each other.

FIGURE 4 Extraction of Am^{III} (1–3), U^{VI} (1'–3') and Pu^{IV} (1"–3") from 0.01 M solutions in HNO$_3$ by 0.05 M RR'P(O)CH$_2$CONEt$_2$ in dichloroethane. RR' = Ph$_2$ (1, 1', 1"); RR' = PhBu (2, 2', 2") and RR' = Bu$_2$ (3, 3', 3").

^{241}Am^{III}, $^{152-154}$Eu^{III}, ^{233}U^{VI}, ^{239}Pu^{IV}
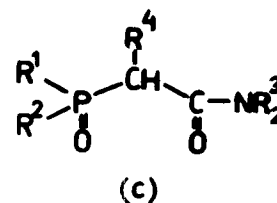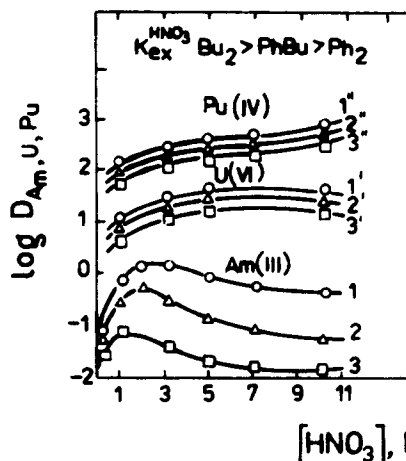
Extraction of Am^{III}, U^{VI} and Pu^{IV} by 0,05M dichloroethane solutions of reagents 1- Ph$_2$P(O)CH$_2$CONEt$_2$, 2- PhBuP(O)CH$_2$CONEt$_2$ and 3 - Bu$_2$P(O)CH$_2$CONEt$_2$ from HNO$_3$ soluttons.

(c)

Trivalent transplutonium element atoms are larger than tetravalent plutonium or hexavalent uranium. Selective extractants for these atoms should be sought among ligands with a substantially larger distance between donor centers than with alkylene diphosphine dioxides and carbamoylmethyl phosphine oxides studied earlier, all other parameters being comparable. We next turned our attention to isomeric xylene derivatives (Scheme 4). In these ligands, donor centers are anchored to the rigid planar xylene bridge. This should undoubtedly result in selectivity of binding cations to complexes.

First, necessary conformational calculations were made. Because of ligand complexity, we had to apply the technique with so-called penalty functions of the quasi-elastic law type,

$$F = K(l_i - l_o)^2$$

They imposed certain geometrical limitations [23]. Here l_i was a variable distance between ligand donor oxygen and metal atoms, and l_o was a present value. The penalty function was added to the conformational energy and the sum was minimized with respect to all variables:

$$U_{conf} = U_{nb} + U_{tors} + U_{el} + U_{ang} + F$$

If the limitation conditions are met, $l_i = l_o$, the penalty function is zero. The calculated results are

TABLE 2 Separation Factor f for Extraction of U^{VI}, Pu^{IV}, Am^{III}, and Eu^{III} from HNO$_3$ into Dichloroethane

R, R'	f(U/Am)	f(Pu/Am)	f(Am/Eu)
R$_2$P(O)CH$_2$CONEt$_2$; 0.05 M; HNO$_3$ 5 M			
Ph	40	400	—
Ph, Bu	100	2000	—
(BuO)$_2$	250	2500	—
Ph, Bu	260	2600	—
Bu$_2$	1250	20000	—
Ph$_2$P(O)CH(R)CONEt$_2$; 0.1 M; HNO$_3$ 3 M			
H	10	—	1.70
C$_7$H$_{15}$	26.3	75.8	1.15
CH$_3$	140	282	2.13
Cl^a	1580	1770	1.50
Cl$_2$^{b}	450	—	2.00

^{a} Concentration C = 0.05 M
^{b} Group CCl$_2$

TABLE 3 A Comparison of Selectivity Factors for Extraction of U^{VI}, Pu^{IV}, and Am^{III} by Extractants of Two Groups

Extractant	f(U/Am)	f(Pu/Am)
cis-Ph$_2$P—CH=CH—PPh$_2$ $\parallel$O $\parallel$O	100	240
R$_2$P—CH=CH—C—NEt$_2$ $\parallel$O $\parallel$O	40–1,250	400–20,000
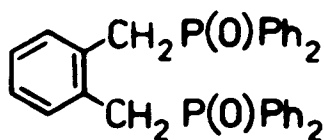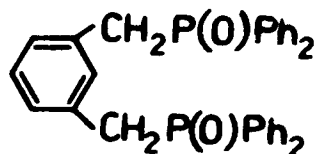
SCHEME 4

illustrated by Figure 5, where U_{conf} is given as a function of l_o. It can be seen that the curve has a deep minimum at $l_o = 2.85$ Å for ligand (XVI), which indicates the ligand to be selective and corresponds well to l_o for uranium (2.6 to 2.8 Å). Energy increases rapidly with l_o. For compound (XVII), the curve has a fairly flat slope over a large range of abscissa values and only rises sharply when l_o becomes smaller than ca 3 Å. According to the calculation results, this ligand can hardly be selective, but it should avoid small cations. In fact, ligand (XVI) selectively extracts U^{VI} rather than americium: in extraction from 3 M nitric acid into chloroform, the separation factor, $f(U/Am)$, is equal to 30,000. At the same time, ligand (XVII) shows only low selectivity, $f(U/Am) = 42$. It, however, extracts americium better than the preceding one does. The con-

formations of both ligands involved in the formation of complexes are shown in Figure 6 for $l_o = 3$ Å. Energetically, this conformation of compound (XVII) costs 2.5 kJ/mol higher energy than with (XVI).

A substantial difference in the extraction properties of ortho- and meta-xylene derivatives prompted us to examine structures of this type in more detail [25]. Synthesized polydiphenylphosphinylmethyl benzenes are listed in Table 4 together with respective separation factors f determined for extraction of uranium, americium, plutonium, and europium from 0.025 M nitric acid solutions into chloroform.

These data show all the ligands to be separated into two groups. The first one includes compounds with separation factors on the order of 10^3 to 10^4 for the pairs uranium/americium and plutonium/

FIGURE 5   The dependence of U_{conf} on l_o for extractants XVI and XVII; l_o in Å, U_{conf} in kJ/mol.
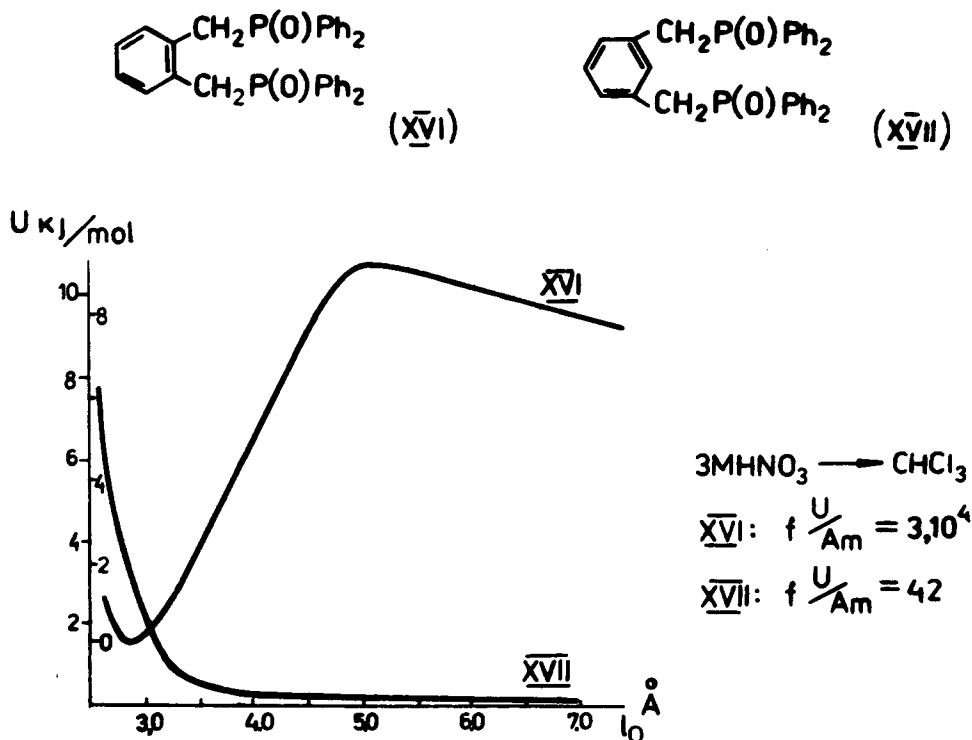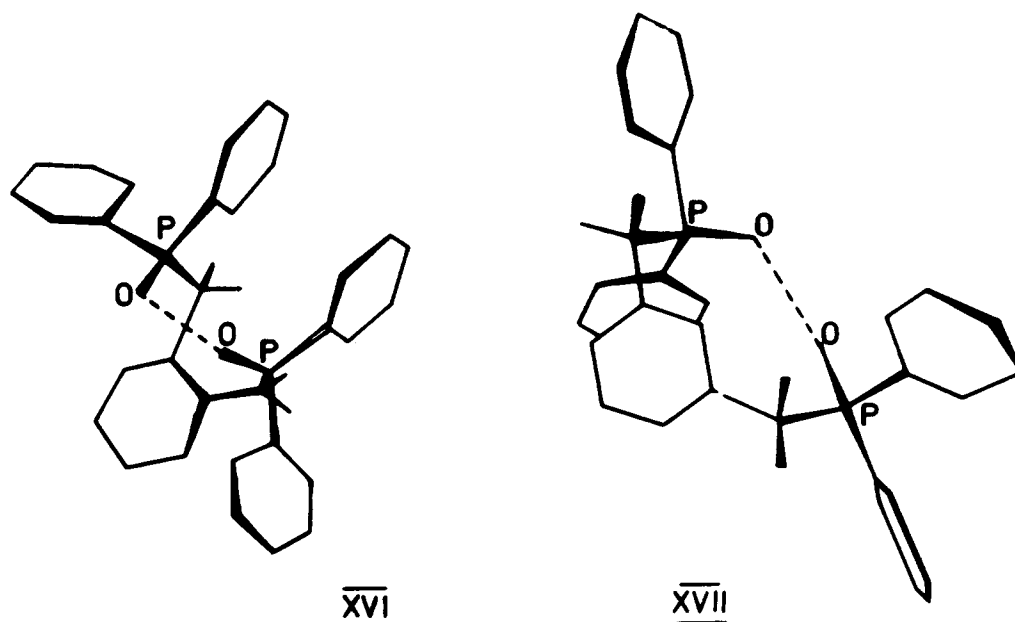
Complex forming conformations of ligands $\overline{XVI}$ and $\overline{XVII}$.

FIGURE 6 Conformation of extractants XVI and XVII with l_o 3 Å.

americium, but fully incapable of separating americium and europium. The other group includes ligands with comparatively low uranium/americium and plutonium/americium separation factors (not higher than 10^2, more often in the range of 20 to 60). They, however, show somewhat higher factors, of 4 to 6, for europium/americium. There seems to

be no doubt that the preference given by ortho-type ligands to small uranium (VI) and plutonium (IV) cations (r = 0.80 and 0.93 Å, respectively) rather than large americium (r = 1.00 Å) is determined by the factor mentioned above, the small l_o value (2.85 Å). The low selectivity of the meta-series compounds is also easy to understand. According to the

TABLE 4 Separation Factors $f = D_i/D_j$ for Pairs $U^{VI}-Am^{III}$, $Pu^{IV}-Am^{III}$ and $Eu^{III}-Am^{III}$ (extraction from 3 M HNO$_3$ in CHCl$_3$, extractant concentration 0.025 mol/l) ∿ $\equiv$ CH$_2$P(O)Ph$_2$

No.	Extractant	$f\dfrac{U^{VI}}{Am^{III}}$	$f\dfrac{Pu^{IV}}{Am^{III}}$	$f\dfrac{Eu^{IV}}{Am^{III}}$	No.	Extractant	$f\dfrac{U^{VI}}{Am^{III}}$	$f\dfrac{Pu^{IV}}{Am^{III}}$	$f\dfrac{Eu^{IV}}{Am^{III}}$
		Type ortho					Type meta		
XVI		$2.0\ 10^4$	$1.5\ 10^4$	—	XVII		42.0	100	4.0
XVIII		$1.2\ 10^3$	$2.8\ 10^3$	1	XXIII		21.8	40.0	4.0
XIX		$2.5\ 10^3$	$1.0\ 10^3$	1	XXIV		24.0	56.2	6.0
XX		$2.0\ 10^4$	$1.0\ 10^4$	2	XXV		60.0	60.0	5.0
XXI		$6.2\ 10^3$	$1.0\ 10^4$	0.6	XXVI		18.2	12.0	—
XXII		$5.2\ 10^2$	$2.0\ 10^4$	—					

log D values observed in extraction by meta-xylene derivatives, transplutonium elements can nevertheless be ordered into the series

$$Cf > Bk > Cm > Am$$

This ordering coincides with that of decreasing element numbers; ligand XVII is a better extractant for large cations.

In conclusion, I would like to emphasize that it is absolutely necessary to take into consideration steric characteristics of the complex formation process for treating the results of extraction studies, especially with di- and polydentate ligands, and for a rational choice of new ligands, with desired efficiency and selectivity of binding cations to complexes. This point has not received adequate attention as yet.

ACKNOWLEDGMENTS

REFERENCES

[1] B. N. Laskorin, L. A. Fedorova, E. P. Buchikhin, *Khimiya Protsessov Ekstraktsii* (*Chemistry of Extraction Processes*), Moscow, Nauka, p. 66 (1972).

[2] A. M. Rozen, Z. I. Nikolotova, A. A. Vashman, N. A. Kartasheva, Z. N. Nagnibeda, A. S. Skotnikov, P. M. Borodin, Yu. I. Mitchenko, Yu. I. Murinov, Yu. I. Nikitin, *Khimiya Protsessov Ekstraksii* (*Chemistry of Extraction Processes*), Moscow, Nauka, p. 41 (1972).

[3] I. Stray, Solvent Extraction Chemistry, Amsterdam, North-Holland Publ. Comp., p. 7 (1967).

[4] A. M. Rozen, Z. I. Nikolotova, A. A. Vashman, N. A. Kartasheva, Z. N. Nagnibeda, Yu. I. Nikitin, *Khimiya Protsessov Ekstraktsii* (*Chemistry of Extraction Processes*), Moscow, Nauka, p. 48 (1972).

[5] M. I. Kabachnik, B. N. Laskorin, L. E. Bertina, T. Ya. Medved', V. G. Kossykh, K. S. Yudina, Z. A. Berkman, A. M. Nepryakhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 65–72. Correlation has been calculated later.

[6] Z. A. Sheka, K. B. Yatsimirskii, M. A. Ablova, K. S.

Yudina, T. Ya. Medved', M. I. Kabachnik, *Zh. neorg. Khim.*, 16, 1971, 2440.

[7] A. P. Baranov, V. G. Dashevskii, T. Ya. Medved', M. I. Kabachnik, *Teor. i eksp. Khim.*, 13, 1977, 488.

[8] L. I. Arkhipova, Z. A. Berkman, L. E. Bertina, M. I. Kabachnik, V. G. Kossykh, T. Ya. Medved', N. P. Nesterova, Yu. M. Polikarpov, A. M. Rozen, K. S. Yudina, *Doklady Akad. Nauk SSSR*, 209, 1973, 1093.

[9] B. F. Myasoedov, T. Ya. Medved', A. A. Nemodrug, N. P. Nesterova, O. E. Koiro, M. I. Kabachnik, *Doklady Akad. Nauk SSSR*, 217, 1974, 1087.

[10] M. I. Kabachnik, O. E. Koiro, T. Ya. Medved', B. F. Myasoedov, N. P. Nesterova, M. K. Chmutova, *Doklady Akad. Nauk SSSR*, 222, 1975, 1346.

[11] M. K. Chmutova, N. P. Nesterova, O. E. Koiro, B. F. Myasoedov, *Zn. analit. Khim.*, 30, 1975, 1110.

[12] M. I. Kabachnik, Yu. M. Polikarpov, *Zn. org. Khim.*, 58, 1988, 1937.

[13] V. G. Dashevskii, A. P. Baranov, T. Ya. Medved', M. I. Kabachnik, *Teor. i eksp. Khim.*, 14, 1977, 340.

[14] A. P. Baranov, V. G. Dashevskii, T. Ya. Medved', M. I. Kabachnik, *Teor. i eksp. Khim.*, 13, 1977, 488.

[15] K. B. Yatsimirskii, M. I. Kabachnik, E. I. Sinyavskaya, T. Ya. Medved', F. I. Bel'skii, *Teor. i eksp. Khim.*, 12, 1976, 777.

[16] T. Ya. Medved', B. A. Korolev, K. S. Yudina, B. I. Stepanov, M. I. Kabachnik, *Teor. i eksp. Khim.*, 4, 1968, 116.

[17] E. I. Matrosov, M. Yu. Antipin, N. P. Nesterova, T. Ya. Medved', Yu. T. Struchkov, M. I. Kabachnik, *Doklady Akad. Nauk SSSR*, 273, 1983, 1419.

[18] E. I. Matrosov, A. P. Baranov, A. G. Matveeva, N. P. Nesterova, M. I. Kabachnik, in print.

[19] E. G. Il'in, M. E. Ignatov, Yu. A. Buslaev, T. Ya. Medved', N. P. Nesterova, M. I. Kabachnik, *Doklady Akad. Nauk SSSR*, 282, 1985, 126.

[20] W. W. Schulz, L. D. McIsaac, Proceeding of the Intern. Solv. Extract. Conf. (Toronto, 1977) CIM special vol. 21. *The Canadian Inst. of Mining and Metallurgy*, 2, 1979, 619.

[21] T. Ya. Medved', M. K. Chmutova, N. P. Nesterova, O. E. Kocherkova, B. F. Myasoedov, M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2121.

[22] B. F. Myasoedov, M. K. Chmutova, N. E. Kochetkova, O. E. Koiro, G. A. Gribylova, N. P. Nesterova, T. Ya. Medved', M. I. Kabachnik, *Solvent Extraction and Ion Exchange*, 4, 1986, 61–81.

[23] V. G. Dashevskii, A. P. Baranov, T. Ya. Medved', M. I. Kabachnik, *Doklady Akad. Nauk SSSR*, 270, 1983, 355.

[24] G. V. Bodrin, M. I. Kabachnik, N. E. Kochetkova, T. Ya. Medved', B. F. Myasoedov, Yu. M. Polikarpov, M. K. Chmutova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2572.

[25] B. F. Myasoedov, G. V. Bodrin, M. K. Chmutova, N. E. Kochetkova, T. Ya. Medved', Yu. M. Polikarpov, M. I. Kabachnik, *Solvent Extraction and Ion Exchange*, 1, 1983, 689.