Russian Journal of General Chemistry, Vol. 75, No. 7, 2005, pp. 1050–1056. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 7, 2005, pp. 1111–1117.
Original Russian Text Copyright © 2005 by Yarkevich, Turanov, Kharitonov.

Synthesis and Extractive Properties of Dialkylaminomethyl-substituted Dialkylamides of Diphenylphosphinoylacetic Acid

A. N. Yarkevich*, A. N. Turanov, and A. V. Kharitonov***

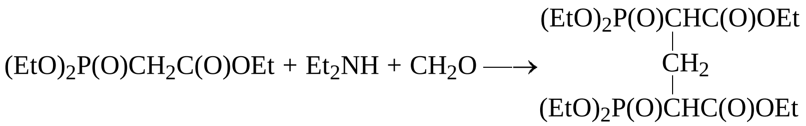
** Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*
*** Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*

Received October 21, 2003

Abstract—Dialkylamides of diphenylphosphinoylacetic acids, dialkylaminomethyl-substituted by the methylene group, were prepared by means of the Mannich reaction from diphenyl(dialkylcarbamoylmethyl)-phosphine oxides or by reaction of the latter compounds with tetraethylmethylenediamine. Extractive ability of the obtained compounds toward U(VI) and Pd(II) in nitrate media was studied.

Alkylation of dialkylamides of diphenylphosphinoylacetic acid by the methylene group is most commonly complicated by the low CH acidity of methylene protons. For this reason, α-alkyl-substituted dialkylamides of diphenylphosphinoylacetic acid are usually prepared starting from potassium derivatives of corresponding dialkylamides [1] or preliminary synthesized α-alkyl-substituted diphenylphosphinoylacetic acids [2]. In the present work we studied feasibility of direct dialkylaminomethylation of certain dialkylamides of diphenylphosphinoylacetic acid for preparing complex-forming agents of a new type.

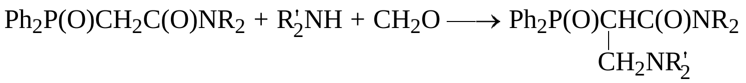
Ethyl (diethoxyphosphinoyl)acetate whose methylene protons exhibit enhanced acidity due to the electron-acceptor effect of the ethoxycarbonyl group reacts with Formalin and diethylamine under Mannich reaction conditions to form a condensation product, diethyl 2,4-bis(diethoxyphosphinoyl)pentane-1,5-dioic acid [3].



$$(EtO)_2P(O)CH_2C(O)OEt + Et_2NH + CH_2O \longrightarrow \begin{array}{c} (EtO)_2P(O)CHC(O)OEt \\ | \\ CH_2 \\ | \\ (EtO)_2P(O)CHC(O)OEt \end{array}$$

Unlike ethyl (diethoxyphosphinoyl)acetate, *N*,*N*-dialkyl(diphenylphosphinoyl)acetamides $Ph_2P(O)CH_2 \cdot C(O)NR_2$ **Ia**–**Ic** [R = Et (**a**), *i*-Bu (**b**), Hex (**c**)] form under analogous conditions α-dialkylaminomethyl-substituted derivatives that combine three types of complex-forming groups in one molecule and, therefore, are perspective to study as extractants.

Amides **Ia** and **Ib** can be converted to dialkylaminomethyl derivatives **IIIa**–**IIIc** under usual Mannich reaction conditions, i.e. by the reaction with equimolar amounts of formaldehyde and dialkylamine at 60–80°C (method *a*).



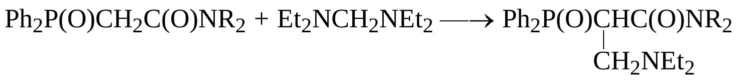
$$Ph_2P(O)CH_2C(O)NR_2 + R'_2NH + CH_2O \longrightarrow \begin{array}{l} Ph_2P(O)CHC(O)NR_2 \\ \qquad\quad | \\ \qquad\quad CH_2NR'_2 \end{array} \qquad (a)$$

Ia, Ib **IIa, IIb** **IIIa**–**IIIc**

1070-3632/05/7507-1050 ©2005 Pleiades Publishing, Inc.

Under more rigid conditions that are required for transformation of much less reactive dialkylamides **Ib** and **Ic** bearing bulky substituents on the nitrogen atom, especially in reaction with dibutylamine, additional signals appeared in the ^{31}P NMR spectra of the reaction mixture. This fact is probably explained by partial decomposition of reaction products at high temperatures. In detail, in the synthesis of compound **IIIb** in boiling ethanol, along with the target product, its decarbamoylation product $Ph_2P(O)CH_2CH_2NBu_2$ (δ_P 32.04 ppm) and diphenyl(vinyl)phosphine oxide $Ph_2P(O)CH{=}CH_2$ (δ_P 25.00 ppm, mp 125–126°C) formed by deamination of the latter were isolated by column chromatography and identified by ^{1}H NMR spectroscopy.

In an alternative procedure (method *b*) we employed preliminarily prepared tetraethylmethylenediamine **IV**, bp 165–167°C, as dialkylaminomethylating agent. This approach allowed reaction with the starting dialkylamides to be accomplished at higher temperatures (120–140°C) in the absence of solvent. Method *b* was used to prepare products **IIIa, IIIc,** and **IIId**.



$$Ph_2P(O)CH_2C(O)NR_2 + Et_2NCH_2NEt_2 \longrightarrow Ph_2P(O)\underset{\displaystyle CH_2NEt_2}{\underset{|}{C}}HC(O)NR_2 \qquad (b)$$

Ia–Ic **IV** **IIIa, IIIc, IIId**

I, R = Et (**a**), *i*-Bu (**b**), Hex (**c**); **II**, R' = Et (**a**), Bu (**b**); **III**, R = R' = Et (**a**), R = Et, R' = Bu (**b**), R = *i*-Bu, R' = Et (**c**), R = Hex, R' = Et (**d**).

In the ^{31}P NMR spectra of the reaction mixtures we observed, along with the main signals of the starting (amide) and final (aminoamide) products, an admixture signal at δ_P 25–26 ppm. This signal was assigned to the phosphine oxide $Ph_2P(O)CH{=}CH_2$ that is also probably formed by partial decomposition of compounds **IIIa**–**IIIc** under the reaction conditions. At usual temperatures, the resulting aminoamides are stable. They are crystalline (**IIIa, IIIc**) or oily (**IIIb, IIId**) colorless substances. Their yields, methods of synthesis, melting points, and ^{1}H and ^{31}P NMR spectra are listed in Table 1.

In the present work we studied the extractive ability of the synthesized dialkylaminomethyl-substituted dialkylamides of diphenylphosphinoylacetic acid toward U(VI) and Pd(II) in nitrate media.

From the 1,2-dichloroethane–water distribution data for compounds **Ia** and **IIIa** (Figs. 1, 2, and 3) it follows that dialkylaminomethyl-substituted extractant **IIIa** is more lipophilic than unsubstituted dialkylamide **Ia**. It is noticeable that the distribution coefficient *D* of extractant **IIIa** increases with its concentration in the organic phase. This is evidently connected with partial dimerization of **IIIa** in the organic phase with the dimerization constant K_2 [Eq. (1), the components of the organic phase are upperlined].

$$2\bar{L} \xrightleftarrows{K_2} \bar{L}_2,\ K_2 = [\bar{L}_2]/[\bar{L}]^2. \qquad (1)$$

In this case, the phase distribution of an extractant is described by Eq. (2), where P_L is the distribution constant of the monomeric form of the extractant.

$$D = P_L + 2K_2P_L^2[L]. \qquad (2)$$

The values $P_L = 68 \pm 3$ and $K_2 = 5.5 \pm 0.3$ for compound **IIIa** in 1,2-dichloroethane were calculated by the least-squares procedure with the data in Fig. 1, curve *2*. In the water–macroporous sorbent system, extractant **IIIa** scarcely dimerizes in the concentration range under study, and the distribution constant of the monomeric form P_L increases to 270 ± 15.

The effect of the nature of the organic solvent on the extraction of U(VI) with compound **IIIa** from nitrate solutions was studied (Table 2). The highest D_U value was obtained with nitrobenzene as solvent. The weaker uranium extraction in the presence of chloroform is evidently connected with the fact that the activity of the extractant in the organic phase is decreased due to $P{=}O\cdots HCCl_3$ hydrogen bonding. Note that the extraction of uranium with low-polarity solvents (hexane, CCl_4) is not weakened, whereas the use of such solvents in the case of unsubstituted carbamoylmethylphosphine oxides results in a much weaker extraction [5].

Increase in the concentration of NH_4NO_3 in the aqueous phase enhances extraction of uranium into the organic phase (Fig. 2), which is characteristic of the extraction of uranyl nitrate solvates by Eq. (3).

Table 1. Yields, melting points, and ^{1}H and ^{31}P NMR spectra of compounds **IIIa–IIId**

Comp. no.	Yield, % (synthesis method)	mp, °C (hexane)[a]	^{1}H NMR spectrum, δ, ppm					^{31}P NMR spectrum, δ_P, ppm
			Alk$_2$NC=O	Alk$_2$N	PCH, m	PCCH$_2$, br. m	Ph	
IIIa	75 (*a*) 71 (*b*)	64–65	0.84 t (3H), 0.89 t (3H) (2CH$_3$); 3.26 q (2H), 3.34 q (2H) (2CH$_2$)	0.96 t (6H, 2CH$_3$); 2.32 m (2H), 2.42 m (2H) (CH$_2$NCH$_2$)	3.80	3.00	7.46 m (6H), 7.88 m (2H), 8.30 m (2H)	29.93
IIIb	63 (*a*)	[b]	0.86 t (6H, 2CH$_3$); 2.34 m (2H), 2.42 m (2H) (CH$_2$NCH$_2$)	0.88 t (6H, 2CH$_3$); 1.22 m (8H, 2CH$_2$)$_2$; 3.12 m (2H), 3.32 m (2H) (2CH$_2$)	3.78	2.95	7.48 m (6H), 7.90 m (2H), 8.30 m (2H)	30.55
IIIc	74 (*a*)	89–92 78 (*b*)	0.78 m (6H, 2CH$_3$); 0.96 m (6H, 2CH$_3$); 1.78 m (1H), 1.94 m (1H) (2CH); 2.82 m (2H), 3.18 m (2H) (2CH$_2$)	0.90 t (6H, 2CH$_3$); 2.32 m (2H), 2.52 m (2H) (CH$_2$NCH$_2$)	3.82	3.08	7.48 m (6H), 7.90 m (2H), 8.26 m (2H)	29.41
IIId	66 (*b*)	[b]	0.88 m (6H, 2CH$_3$); 1.24 m (16H, (2CH$_2$)$_4$; 3.12 m (2H), 3.32 m (2H) (2CH$_2$)	0.88 m (6H, 2CH$_3$); 2.46 m (4H) (CH$_2$NCH$_2$)	3.80	2.92	7.48 m (6H), 7.90 m (2H), 8.30 m (2H)	30.20

[a] Solvent for crystallization. [b] Oil.

$$UO_2^{2+} + 2NO_3^- + n\overline{L} \rightleftarrows \overline{UO_2(NO_3)_2L_n} \qquad (3)$$

The extraction of U(VI) from nitric acid solutions is appreciably weaker (Fig. 2), which is connected with extractant–HNO$_3$ complex formation in the organic phase and the resulting decrease in the concentration of the free extractant.

The U:L stoichiometric ratio in the extracted uranyl nitrate solvate, as determined from the bilogarithmic dependence of D_U on extractant concentration in dichloroethane, is 1:2 for all the compounds studied (Fig. 3). At high concentrations of **IIIa** in the organic phase, the slope of the $\log D_U$–$\log C_L$ dependence decreases (Fig. 3, curve *5*). This can be connected both with the decrease of the fraction of the monomeric form of the extractant with increasing total concentration of the latter in the organic phase, as well as with the formation of less hydrophobic monosolvates $UO_2(NO_3)_2L$ with increasing concentration of the extractant in the aqueous phase. The dependence of D_U on extractant concentration in equilibrium phases is given by Eq. (4), where $\beta_{1,2}$ are the stability constants of uranyl nitrate solvates and $P_{UO_2(NO_3)L_2}$, distribution constant of extracted solvate.

Table 2. Distribution coefficient of U(VI) on extraction with 0.01 M solutions of compound **IIIa** from 4 M NH$_4$NO$_3$ solutions

Solvent	D_U	Solvent	D_U
Nitrobenzene	5.54	Hexane	0.74
Toluene	1.29	1,2-Dichloroethane	0.74
1,2-Dichlorobenzene	1.14	Chloroform	0.28
CCl$_4$	0.78		

$$D_U = \frac{\beta_2 P_{UO_2(NO_3)_2L_2}[\overline{L}]^2[NO_3^-]^2}{P_L^2\ (1 + \beta_1[L][NO_3^-]^2 + \beta_2[L]^2[NO_3^-]^2)}. \qquad (4)$$

At a constant NH$_4$NO$_3$ concentration in the aqueous phase, the highest D_U value corresponds to the distribution constant of extracted solvate ($P_{UO_2(NO_3)_2L_2}$). For the complex of U(VI) with **IIIa** in

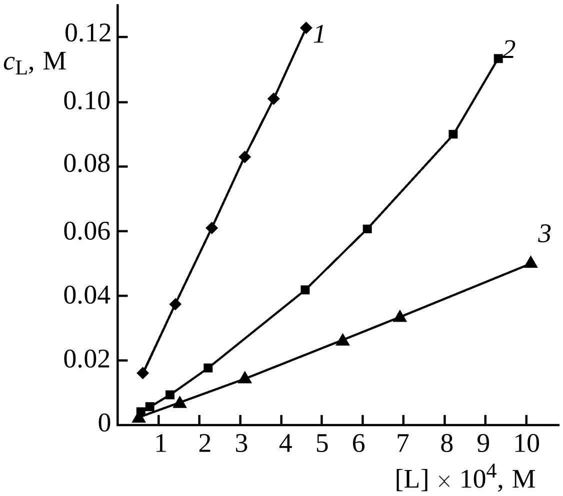


Fig. 1. Dependence of the equilibrium concentration of compounds (*1, 2*) **IIIa** and (*3*) **Ia** in (*2, 3*) 1,2-dichloroethane or (*1*) macroporous sorbent phase (**I**) on the equilibrium concentration of compounds **Ia** and **IIIa** in the aqueous phase.

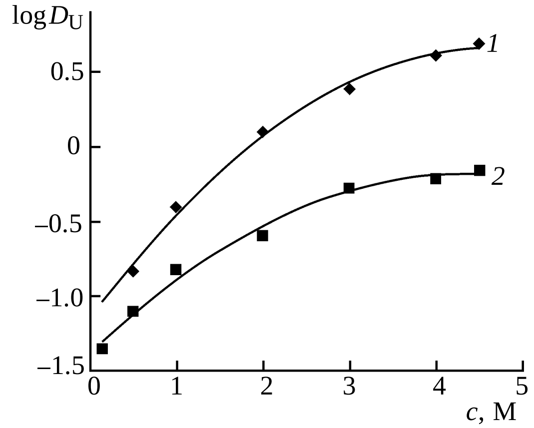


Fig. 2. Dependence of the distribution coefficient of uranium on the concentration of (*1*) NH_4NO_3 and (*2*) HNO_3 in the aqueous phase on the extraction of uranium with 0.025 M solutions of compound **IIIa** in 1,2-dichloroethane.

dichloroethane it is equal to 26.3 ± 2.5. More effective extraction of uranium with extractant **IIIa** is achieved by application of the latter on a macroporous sorbent (Vofatit ER 60 styrene–divinylbenzene copolymer) (Fig. 3, plot *1*), which is explained by increased $P_{UO_2(NO_3)_2L_2}$ in such systems. The advantages of impregnated sorbent extraction of metal complexes from aqueous solutions over liquid extraction have repeatedly discussed in the literature [6–9].

The alteration of the extractive activity of compounds **IIIa**–**IIId** toward uranium is connected with the alteration of the stability constants of the uranyl nitrate disolvates formed, as well as by the alteration of the distribution constants of these solvates. As the lipophilicity of the ligand involved in complex formation increases with increasing size of the hydrocarbon radicals on the amide nitrogen atoms and the dialkylaminomethyl fragment, the extractive ability increases in the series **IIIa** < **IIIb** < **IIId**. Replacement of ethyl radicals at the amide nitrogen atom (compound **IIIc** by isobutyls (compound **IIIa**) increases the lipophilicity of the ligand but adversely affects uranium extraction, which is probably connected with steric hindrances to complex formation and decreased stability of the corresponding uranyl nitrate disovates.

(Diethylcarbamoylmethyl)diphenylphosphine oxide (**Ia**) more effectively extracts U(VI) than reagent **IIIa** (Fig. 3). This fact agrees with the notion that Pearson's hard ion UO_2^{2-} is extracted as a coordinately solvated uranyl nitrate. The decreased extraction of U(VI), Am(III) and Eu(III) from nitric acid solutions on introduction of alkyl, benzyl, diethylaminopropyl, and some other substituents into the methylene bridge of tetraphenylmethylene dioxide and diphenyl(dialkylcarbamoylmethyl)phosphine oxides may be explained by restricted conformational mobility of ligands involved in complex formation [1, 11]. Furthermore, the fairly high basicity of the nitrogen atom in the $CH_2NR'_2$ fragment of **IIIa**–**IIId** enhances HNO_3 extraction with these reagents compared to unsubstituted

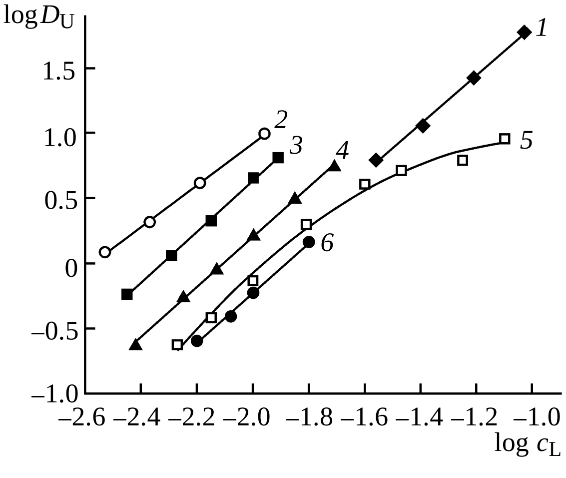


Fig. 3. Dependence of the distribution coefficient of uranium on the initial concentrations of compounds (*2*) **Ia**, (*1, 5*) **IIIa**, (*4*) **IIIb**, (6) **IIIc**, and (*3*) **IIIg** in (*3–6*) dichloroethane or (*1*) polymeric sorbent phase on the extraction of uranium from 4 M solution of NH_4NO_3.

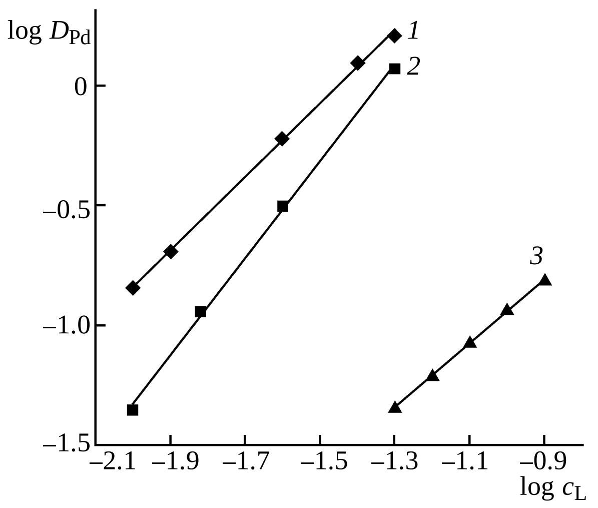


Fig. 4. Dependence of the distribution coefficient of palladium on the concentration of (*1*) compound **IIIa**, (*2*) trioctylamine, and (*3*) compound **Ia** in 1,2-dichloroethane on extraction from 0.15 M HNO_3 solution.

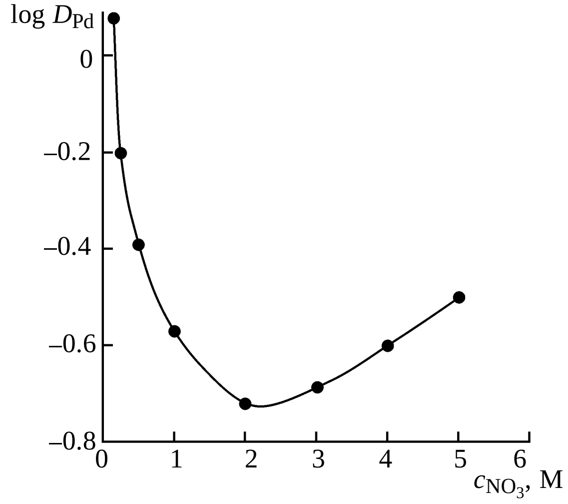
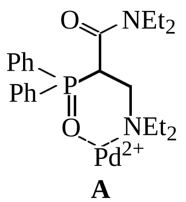


Fig. 5. Dependence of the distribution coefficient of palladium on the concentration of HNO_3 in the aqueous phase on extraction with 0.05 M solution of compound **IIIa** in chloroform.

dialkylamides **Ia**–**Ic**, which appreciably decreases the concentration of the free extractant in the organic phase and decreases D_U [Eq. (4)].

On the other side, introduction of the CH_2NEt_2 fragment in amide **Ia** enhances extraction of Pearson's soft ion Pd^{2+} with reagent **IIIa** (Fig. 4). The apparent solvation number for the extraction of Pd(II) with this compound, estimated by the equilibrium shift method, is 1.5, which implies extraction of 1 : 1 and 1 : 2 Pd : L (**IIIa**) complexes. Under these experimental conditions, D_{Pd} for the extraction with compound **IIIa** is slightly higher than for the extraction of palladium with trioctylamine (Fig. 4). This result is probably connected with the formation of chelate ring **A** on the extraction of palladium nitrate monosolvate. Such chelate structures were previously used to explain enhanced palladium extraction with tetraalkylethylenes [12].



A

On the extraction of palladium with compound **IIIa** the distribution coefficient of palladium decreases with increasing concentration of nitric acid in the aqueous phase (Fig. 5), on account of competition of HNO_3 for the extractant. When the concentrations of HNO_3 is higher than 2 M, the D_{Pd} value slightly increases, probably, because the anionic forms of palladium are extracted with the protonated extractant in the form of the $[Pd(NO_3)_4]^{2-}(HL^+)_2$ complex by the mechanism of extraction with amine salts [13]. Evidence for the formation of such an associate in the organic phase comes from the observation in the electronic absorption spectrum, along with the band at λ 410 nm, of one more band at λ 325 nm. According to [14], this additional band suggests that palladium is extracted with amines in the form of a double salt including the $[Pd(NO_3)_4]^{2-}$ anion.

It is known that solvation of an amine salt with nucleophilic reagents, associated with charge transfer from the reagent on the hydrogen atom of the amine salt, should increase the extractive ability of the latter [13]. Actually, in the presence of diphosphine dioxide $Ph_2P(O)(CH_2)_5P(O)Ph_2$ (S) in the organic phase, a synergistic effect is observed on palladium extraction with a mixture of reagents **IIIa** and S (Fig. 6). The method of isomolar series was used to show the highest synergism coefficient $A = D/(D_1 + D_2)$ (D_1, D_2, and D are the distribution coefficients for palladium extraction with individual reagents and their mixture, respectively) is observed at a 1 : 1 reagent molar ratio in the organic phase (Fig. 6). It can be proposed that the complex $[Pd(NO_3)_4](HL)_2$ extracted with compound **IIIa** in the presence of dioxide S is transformed in an ionic associate containing S in the anionic part of the complex.

$$\overline{[Pd(NO_3)_4]^{2-}(HL^+)_2} + \overline{S}$$

$$\rightleftarrows \overline{[Pd(NO_3)_3S]^{-}(HL^+)} + \overline{HL\cdot NO_3}. \qquad (5)$$

This process is favored by increased concentration of compound S in the organic phase and decreased concentration of nitric acid in the equilibrium aqueous phase. Substitution of the NO_3^- ligand in the inner coordination sphere of the complex Pd(II) anion with S increases hydrophobicity of the extracted anionic associate and may be one of the reasons for the observed synergistic effect.

The presented data show that substitution of the hydrogen atom in the methylene bridge of *N,N*-dialkyl(diphenylphosphinoyl)acetamide with a dialkylaminomethyl group may both decrease and increase the extractive ability of the resulting compound, depending on the nature of the ion to be extracted.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were registered for $CDCl_3$ solutions on a Bruker CXP spectrometer at 200 and 81 MHz, respectively, against internal TMS and external H_3PO_4. The melting points were measured on a Boetius PNMK-05 device. The concentration of uranium in the starting and equilibrium aqueous solutions was measured on a KFK-2MP photocolorimeter in the presence of Arsenazo III, and the concentration of palladium in the aqueous solutions was measured on the same device in the presence of nitroso-R-salt [15]. The concentrations of extractants **Ia** and **IIIa** in the aqueous phase were determined spectrophotometrically at λ 270 nm on an SF-26 spectrophotometer. The electronic absorption spectra of the extracts were obtained on a Specord UV VIS spectrophotometer.

Extraction equilibria were studied using nitrobenzene, toluene, 1,2-dichlorobenzene, CCl_4, hexane, 1,2-dichloroethane, and chloroform of pure or analytical grades. The **IIIa**-impregnated sorbent was prepared on a Vofatit EP 60 (Germany, Bitterfeld) nonionogenic macroporous styrene–divinylbenzene copolymer matrix. The principal characteristics of the matrix are reported in [16]. The procedure of application of extractant **IIIa** on Vofatit EP 60 is described in [17].

The aqueous solutions of uranyl nitrate with the initial concentration 5×10^{-4} M were prepared from the standard solutions of $UO_2(NO_3)_2$, NH_4NO_3, and HNO_3, prepared from ultrapure grade chemicals. The initial solutions of palladium nitrate were prepared by dissolution of metallic palladium (palladium content 99.12%) in 3 M aqueous HNO_3 at elevated temperature and subsequent dilution of the resulting solution with water to a concentration of Pd^{2+} 5×10^{-4} g-ion/l.

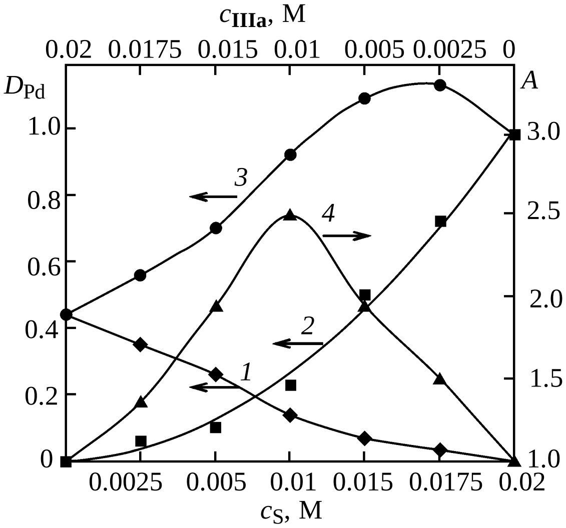


Fig. 6. Extraction of palladium from 0.15 M HNO_3 solutions of (*3*) compound **IIIa**, (*2*) $Ph_2P(O)(CH_2)_5 \cdot P(O)Ph_2$, and (*1*) their isomolar mixtures in 1,2-dichloroethane. (*4*) Synergism coefficient *A*.

The extraction and sorption experiments were carried out at 18±2°C a 1:1 ratio of the organic and aqueous phases for extraction and a 10:1 ratio of the volume of the aqueous phase and the weight of the sorbent for sorption. The phases were stirred for 1 h until constant distribution coefficients.

The synthesis of $Ph_2P(O)CH_2)_5P(O)Ph_2$ [18] and *N,N*-dialkyl(diphenylphosphinoyl)acetamides **Ia, Ic** [2] and **Ib** [19] was described previously.

***N,N*-Diethyl-3-(diethylamino)-2-(diphenylphosphinoyl)propionamide (IIIa)**. *a.* A mixture of 1.58 g of dialkylamide **Ia**, 0.73 g of diethylamine **IIa**, and 2 ml of 30% aqueous Formalin was stirred for 3 h at 60°C. After cooling to room temperature, the reaction mixture was extracted with chloroform (3 × 15 ml). The organic extracts were combined, washed with water, and dried over sodium sulfate. The solvent was removed in a vacuum, and the product was purified by column chromatography on neutral alumina, eluent 15:1 hexane–2-propanol, to obtain 1.41 g of compound **IIIa**, yield 75%.

b. A mixture of 1.58 g of dialkylamide **Ia** and 1.58 g of $Et_2NCH_2NEt_2$ (**IV**) was heated in an evacuated ampule at 130°C for 2 h. Excess diamine was removed in a vacuum. The reaction mixture was cooled, and the product was purified by column chromatography on neutral alumina, eluent 15:1 hexane–2-propanol to obtain 1.41 g (71%) of compound **IIIa**.

***N,N*-Diethyl-3-(dibutylamino)-2-(diphenylphosphinoyl)propionamide (IIIb)**. A mixture of 0.63 g of dialkylamide **Ia**, 0.52 g of dibutylamine **IIb**, and 0.5 ml of 30% aqueous Formalin in 2 ml of ethanol was stirred under slight reflux for 3 h. The reaction mixture was cooled to room tempeature and extracted with chloroform. The combined organic fractions were washed with water and dried over sodium sulfate. The solvent was removed in a vacuum, and the residue was extracted with dry hexane to remove diphenyl(vinyl)phosphine oxide (0.07 g, yield 16%). The organic extract was concentrated and subjected to column chromatography on neutral alumina. Elution with hexane gave 0.09 g (12%) of $Ph_2P(O)CH_2CH_2 \cdot NBu_2$, and elution with 20 : 1 hexane–2-propanol gave 0.57 g of compound **IIIb**, yield 63%.

***N,N*-Diisobutyl-3-(diethylamino)-2-(diphenylphosphinoyl)propionamide (IIIc)** was obtained analogously to compound **IIIa** by method *a* from 0.93 g of diisobutylamide **IIIb**, 0.73 g of Et_2NH, and 1 ml of 30% aqueous Formalin (60°C, 3 h), and by method *b* from 0.93 g of diisobutylamide **IIIb** and 0.79 g of diamine **IV** (140°C, 6 h).

***N,N*-Dihexyl-3-(diethylamino)-2-(diphenylphosphinoyl)propionamide (IIId)** was obtained analogously to compound **IIIa** by method *b* from 1.07 g of dihexylamide **IIIc** and 0.79 g of diamine **IV** (120°C, 6 h).

ACKNOWLEDGMENTS

The authors express their sincere gratitude to V.O. Zavel'sky and A.N. Pushin for registration and discussion of the NMR spectra.

REFERENCES

1. Kochetkova, N.E., Koiro, O.E., Nesterova, N.P., Medved', T.Ya., Chmutova, M.K., Myasoedov, B.F., and Kabachnik, M.I., *Radoikhimiya*, 1986, vol. 28, no. 3, p. 338.
2. Turanov, A.N., Karandashev, V.K., Kharitonov, A.V., Lezhnev, A.N., Safonova, Z.V., Yarkevich, A.N., and Tsvetkov, E.N., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 7, p. 1109.
3. Petrov, K.A., Chauzov, V.A., and Kostina, L.P., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 3, p. 704.
4. Bondarenko, N.A. and Tsvetkov, E.N., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 7, p. 1533.
5. Rozen, A.M., Nikiforov, A.S., Nikolotova, Z.I., and Kartasheva, N.A., *Dokl. Akad. Nauk SSSR*, 1986, vol. 286, no. 3, p. 667.
6. Flett, D.S., *Chem. Ind.*, 1977, no. 6, pp. 641–646.
7. Meretukov, M.A., *Ispol'zovanie impregnirovannykh materialov dlya izvlecheniya i rasdeleniya tsvetnykh metallov* (Use of Impregnated Materials for Extraction and Separation of Nonferrous Metals), TsNIIEITsM Reviews, 1980, no 3, p. 49.
8. Warshawsky, A., *Solv. Extr. Ion Exch.*, 1981, vol. 8, p. 229.
9. Cortina, J.L., and Warshawsky, A., *Solv. Extr. Ion Exch.*, 1997, vol. 13, p. 195.
10. Rozen, A.M. and Krupnov, V.V., *Usp. Khim.*, 1996, vol. 65, no. 11, pp. 1052–1079.
11. Shadrin, A.Yu., Smirnov, I.V., Kiseleva, R.N., Nesterova, H.P., Polikarpov, Yu.M., and Kabachnik, M.I., *Radiokhimiya*, 1993, vol. 35, no. 1, pp. 50–56.
12. Belova, V.V., Khol'kin, A.I., Vasilevich, S.A., Zhidkova, T.I., Medkov, M.A., Shipunov, Yu.A., and Shumilina, E.V., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 11, p. 1856.
13. Shmidt, V.S., *Ekstraktsiya aminami* (Extraction with Amines), Moscow: Atomizdat, 1980, p. 262.
14. Shmidt, V.S., Shorokhov, N.A., and Novikova, S.S., *Zh. Neorg. Khim.*, 1984, vol. 29, no. 3, p. 773.
15. Ginzburg, S.I., Ezerskaya, N.A., Prokof'eva, I.V., Fedorenko, N.V., Shlenskaya, V.I., and Bel'skii, N.K., *Analiticheskaya khimiya platinovykh metallov* (Analytical Chemistry of Platinum Metals), Moscow: Nauka, 1972.
16. Kremenskaya, I.N., Turanov, A.N., Myul', P., and Gle, K., *Zh. Prikl. Khim.*, 1984, vol. 57, no. 1, p. 72.
17. Turanov, A.N., Tsylov, Yu.A., Reznik, A.M., and Kremenskaya, I.N., *Radiokhimiya*, 1984, vol. 26, no. 3, p. 292.
18. Turanov, A.N., Baylun, V.E., Kharitonov, A.V., and Tsvetkov, E.N., *Zh. Neorg. Khim.*, 1994, vol. 39, no. 8, p. 1394.
19. Shvetsov, I.K., Trukhlyaev, P.S., Kalistratov, V.A., Kulyako, V.G., Kharitonov, A.V., Antoshin, A.E., and Tsvetkov, E.N., *Radiokhimiya*, 1989, vol. 31, no. 2, p. 63.