Correlation analysis of "arylic strengthening" of the extraction capacity of bidentate organophosphorus extractants

M. I. Kabachnik,*[a] *B. F. Myasoedov*,[b] *T. A. Mastryukova*,[a]
Yu. M. Polikarpov,[a] *M. K. Chmutova*,[b] *and N. P. Nesterova*[a]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085
[b]*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,*
19 ul. Kosygina, 117975 Moscow, Russian Federation.
Fax: 007 (095) 938 2054

This paper is devoted to the so-called effect of "anomalous arylic strengthening" (AAS) observed upon extraction of a series of elements, mainly actinides and lanthanides, by bidentate neutral organophosphorus compounds (BNOPC). This "anomalous" effect is an increase in the extraction capacity of a reagent when alkyl substituents at the phosphorus atom are replaced with more electronegative aryl groups. The influence of phenyl substituents at the phosphorus atom on the reactivity of organophosphorus compounds of various types was considered. Based on the data on electronic effects of substituents, hypotheses were formulated about the reasons for AAS involving phenyl groups that are biphilic because they have substituents capable of manifesting both donor and acceptor properties depending on several factors such as, *e.g.*, the nature of the reaction center, the character of the attacking reagent, the nature of the solvent, *etc.* When a strong complex of a metal with a phenyl-substituted reagent of BNOPC is formed during extraction, the phenyl groups become donating, and additional strengthening of the complex appears.

Key words: organophosphorus compounds, extraction, complex stability, correlation analysis.

The concept of the "anomalous arylic strengthening" (AAS) has been developed in Refs. 1—5. The study of the extraction of americium(III) and other trivalent transplutonium (TPE) and rare-earth (REE) elements by bidentate organophosphorus reagents of the $R_2P(O)-(CH_2)_n-P(O)R_2$ type has observed an anomaly in the ratio of the extraction capacity and basicity of these substances caused by the replacement of alkyl groups R by aryl groups and by changing the length of the chain of CH_2 groups (n) between phosphorus atoms. It turned out that the replacement of alkyl groups R by aryl groups and decreasing the number of units (n) between donor groups results in an increase in the extraction capacity of these compounds, while the basicity of these extractants, by contrast, decreases. The authors of Refs. 1—5 accepted that phenyl (aryl) groups are more electronegative than alkyl groups (which is correct, generally speaking) and considered the phenomenon discussed to be anomalous, especially as it is not observed in extraction by monodentate organophosphorus reagents.* The authors of Ref. 1 assumed that this type anomaly is caused by the resonance stabilization of a metal complex with a bidentate extractant through aromatization of the six-membered cycle. The assumption that delocalization of the electron density from the aryl groups to the central cycle formed during the formation of a complex with a metal plays a role is favored by the results of the measurements of X-ray electronic and ^{1}H NMR spectra and quantum-chemical calculations[4,5] as well as by the disappearance of the effect when aryl substituents are replaced by the groups with the same electronegativity but without the possibility of conjugation, or when the phenyl substituent is separated from the phosphorus atom by a CH_2 group.

Admittedly, the conclusions of the authors of Ref. 1 seemed so convincing that many authors of works on the extraction of actinides by organophosphorus extractants, including us, repeatedly observing the absence of parallelism between the basicity and extraction capacity of bidentate orgnophosphorus extractants and an increase

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* In extraction practice, the ratio of the extraction constants of an element with aryl- and alkyl-substituted reagents, K_{ex}^{Ar}/K_{ex}^{Alk}, is usually accepted as the quantitative estimation of the effect. In particular cases, the ratios of the distribution coefficients of elements for extraction by the same reagents are used, although it is not quite correct (when the concentration of acid in an aqueous medium is fairly high, the binding of the reagent with the acid is not taken into account).

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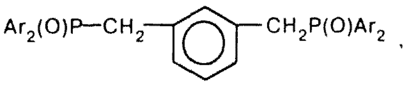
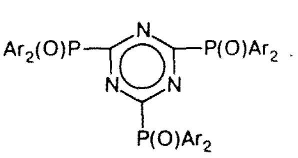
in the extraction capacity on going from alkyl to aryl derivatives, used the idea of AAS. The development of works on extraction of elements by bidentate (and polydentate) neutral organophosphorus compounds (BNOPC) enlarged substantially the range of compounds, extraction by which results in the so-called AAS effect.

For example, it turned out that the formation of six- and seven-membered chelate cycles (*via* CH_2 and CH=CH bridges between the P=O groups, respectively) is not necessary for the appearance of the effect. The effect was also observed in the extraction of trivalent transplutonium and rare-earth elements by bis-[(diaryl)phosphorylmethyl]benzenes,[6,7] in which a benzene ring with methylphosphoryl groups at *meta*-positions serves as the bridge linking the functional groups



and by 2,4,6-tris[diarylphosphoryl]-1,3,5-triazines[8]



The effect was also observed in the extraction of elements by solutions of BNOPC with different types of functional groups, one of which must be a P=O group. The widely known diaryl[dialkylcarbamoylmethyl]phosphine oxides $R_2P(O)CH_2C(O)NR_2'$ [9–11] belong to this group of reagents.

In extraction by these reagents, the effect is observed only when the phenyl group is linked with the phosphorus atom (and not the nitrogen atom).[11] It has been found that the amount of the effect observed depends substantially on the nature of the acid in an aqueous medium. It is especially high in the extraction of elements from solutions of perchloric acid and its salts.[1,12,13]

Based on the rich experimental material, it has been established that a necessary condition for the appearance of the "arylic strengthening" effect of the extraction capacity is the existence of at least two functional groups capable of closing the cycle with a metal in the reagent. At least one of these groups must be a P=O group linked with at least one aryl group.

However, there are published data that allow one to doubt the existence of AAS. Reference 14 is devoted to the extraction capacity of dialkyl- and diaryl(dialkylcarbamoylmethyl)phosphine oxides $R_2P(O)-CH_2-CONR_2'$ with respect to americium ions. The authors of Ref. 14 compared the extraction capacities of these compounds containing R = C_8H_{17} and R = Ph in solvents of different solvating capacities and found that the ratio of the extraction constants $K_{ex}{}^{Oct}/K_{ex}{}^{Ph}$ in weakly solvating media is less than unity, while it is greater than unity in strongly solvating media. In other words, AAS is not observed in weakly solvating media, but it is observed in strongly solvating media. In the first case, aryl groups decrease the extraction, and in the second case, they increase it. Assuming that the intramolecular influence of the phenyl group on the complex-forming capacity of the bidentate ligand is independent of the nature of the solvent, the authors concluded that no AAS exists and reduced the problem to the role of the solvation of extractant molecules by the solvent. Using Shmidt's "dilution parameters" (DL)[15] as a measure of the solvating capacity of solvents, the authors obtained a satisfactory linear dependence $\log K_{ex}^{Oct}/K_{ex}^{Ph}$ on DL (the correlation coefficient was 0.96).

To understand the AAS effect, it is necessary to consider in more detail the influence of phenyl substituents at the phosphorus atom on the reactivity of organophosphorus compounds.

It is noteworthy that the special properties that are imparted to an organophosphorus molecule by the existence of phenyl (aryl) groups at the phosphorus atom were marked repeatedly and long ago,[16,17] especially when the dissociation constants of phosphorus acids containing one or two phenyl groups at the phosphorus atom were compared. The effect observed was explained by the mesomeric influence of phenyl (aryl) groups and its steric dependence. An interpretation of this kind has lately been suggested in the study of the stability constants of the complexes formed by the bidentate reagents $R_2P(O)CH_2P(O)R_2$ with alkali metal halides. In this case, phenyl groups also resulted in higher stability of the complex than alkyl groups did.[18]

According to the electronic effect in organic reactions, aryl groups are typically biphilic. This means that in different situations they can be both electron-withdrawing and electron-releasing groups. This is caused by the high polarizability of their π-electronic system, which, depending on many factors, can donate electron density to the reaction center at the time of a reaction or can, by contrast, accept it. The nature of the reaction center should be the first named among these factors, then the character of the attacking reagent, the existence of substituents in the benzene ring and their nature, the character of the medium, *etc.* The analysis of the combined action of all factors is a rather complicated problem requiring rigorous theoretical consideration.

However, fairly convincing conclusions can be drawn on the basis of $\sigma\rho$-correlation analysis. We have developed[19] a basis for $\sigma\rho$-correlation analysis applicable to the chemistry of organophosphorus compounds. The σ^{Φ} constants for different groups at the phosphorus atoms were derived from experimental data, and numerous good linear correlations between rate constants and equilibrium constants of organophosphorus reactions were revealed from the Hammett equation:

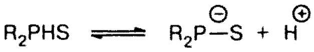
$$\log K = \log K^0 + \rho\Sigma\sigma^{\Phi}.$$

The value and sign of the σ^{Φ} constant characterize entirely the effect of a given substituent at the phosphorus atom. It has been found for phenyl and other aryl groups that their σ^{Φ} constants can vary. They depend first on the number of aryl groups linked to the phosphorus atom and can vary within wide limits in different reactions. In this respect, σ^{Φ} are similar to the σ_p constants of aryl groups in the Hammett equation, which are also rather variable. For example, when the electronic parameter of the reaction center in an organic compound differs slightly from that of carboxyl groups of benzoic acids (this is the reaction series from which the σ constants of the Hammett equation were derived), the σ_p constant of the phenyl group is close to zero. According to Jaffe, σ_p = 0.009, and according to McDaniel and Brown, it is equal to −0.01.[20] The σ constant of the phenyl group changes substantially when the reaction center is nucleophilic, as in the phenoxide ion or in aniline. It is designated as σ^- and can take values of +0.02 (anilines), +0.07 or +0.10 (phenols),[21] and even can reach a value of +0.30.[22] These values of the σ_p constant characterize the phenyl group as an electron acceptor. Of course, this accepting effect is not high: for the typical accepting group, for example, CN, σ^- = +0.88— +0.98, and for the bromide ion, σ^- = +0.25.

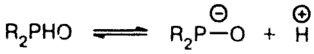
By contrast, when the reaction center is electrophilic, as in the triphenylmethyl cation (Ph_3C^+) or the cumyl cation ($C_6H_5C^+Me_2$), σ_p takes values from −0.07 to −0.35 [21] and even to −0.38.[23] This already indicates pronounced donating properties, which are not exceeded by those, *e.g.*, of the methoxyl group for which σ_p = −0.268 for the ionization of benzoic acids in water.

Thus, under appropriate conditions, the electronegative (according to inductive effects) phenyl group can turn out to be a strong π-donor or a weak π-acceptor.

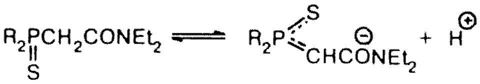
Now let us consider a phenyl group linked to a phosphorus atom. The characteristics of the phenyl group in the correlation analysis of organophosphorus compounds (the standard series is the ionization of RR′POOH type acids) can be determined by the value of σ^{Φ}, which is equal to −0.48 in the dissociation of phenylphosphonic acid $C_6H_5PO_3H_2$ or its acidic esters in water. This constant is very variable and changes under the action of many factors. It depends on the number of phenyl groups at the phosphorus atom and the nature of the reaction center. We will consider below the changes in the σ^{Φ} constant of the phenyl group in the case of two phenyl substituents at the phosphorus atom: they are more indicative than those in the case of one phenyl group (when changes in the constants have the same character but are less pronounced). The examples for the changes in the σ^{Φ} constant of the phenyl group (in the composition of the Ph_2P fragment) upon the acidic dissociation of various PH-, CH-, and OH-acids in accordance with equations (1)—(10) are presented in Table 1.



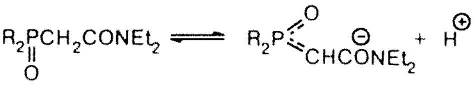
$$R_2PHS \rightleftharpoons R_2P{-}\overset{\ominus}{S} + \overset{\oplus}{H} \qquad (1)$$



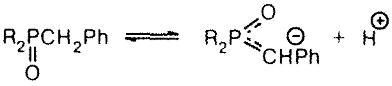
$$R_2PHO \rightleftharpoons R_2P{-}\overset{\ominus}{O} + \overset{\oplus}{H} \qquad (2)$$



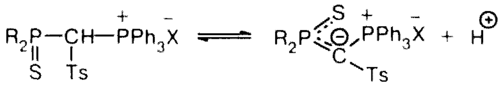
$$R_2\underset{\|}{\overset{}{P}}(S)CH_2CONEt_2 \rightleftharpoons R_2P(\cdots S)(\cdots \overset{\ominus}{C}HCONEt_2) + \overset{\oplus}{H} \qquad (3)$$



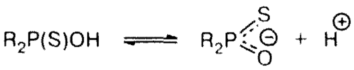
$$R_2P(O)CH_2CONEt_2 \rightleftharpoons R_2P(\cdots O)(\cdots \overset{\ominus}{C}HCONEt_2) + \overset{\oplus}{H} \qquad (4)$$



$$R_2P(O)CH_2Ph \rightleftharpoons R_2P(\cdots O)(\cdots \overset{\ominus}{C}HPh) + \overset{\oplus}{H} \qquad (5)$$

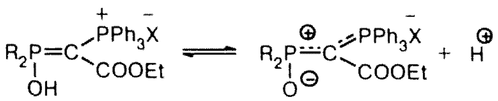


$$R_2P(S){-}CH(Ts){-}\overset{+}{P}Ph_3\overset{-}{X} \rightleftharpoons R_2P(\cdots \overset{+}{S})(\cdots\overset{\ominus}{C}(Ts)PPh_3\overset{-}{X}) + \overset{\oplus}{H} \qquad (6)$$

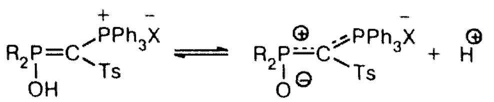


$$R_2P(S)OH \rightleftharpoons R_2P(\cdots S)(\cdots O)^{\ominus} + \overset{\oplus}{H} \qquad (7)$$

$$R_2P(S)OH \rightleftharpoons R_2P(\cdots S)(\cdots O)^{\ominus} + \overset{\oplus}{H} \qquad (8)$$



$$R_2\overset{+}{P}(OH){=}C(\overset{+}{P}Ph_3\overset{-}{X})COOEt \rightleftharpoons R_2\overset{\oplus}{P}(O^{\ominus}){\cdots}C(PPh_3\overset{-}{X})COOEt + \overset{\oplus}{H} \qquad (9)$$



$$R_2P(OH){=}C(\overset{+}{P}Ph_3\overset{-}{X})Ts \rightleftharpoons R_2\overset{\oplus}{P}(O^{\ominus}){\cdots}C(PPh_3\overset{-}{X})Ts + \overset{\oplus}{H} \qquad (10)$$

Ts = $SO_2C_6H_4CH_3$

As can be seen from Table 1, the values of the σ^{Φ} constant of the phenyl group vary over a wide range

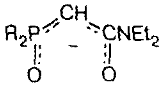
Table 1. Constants σ^{Φ} of the phenyl group in a series of reactions of dissociation of OH-, SH-, CH-, and NH-acids

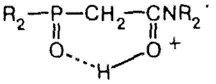
Reaction	Type	Medium	σ^{Φ}	Ref.*
1	PH	DMSO	+0.08	24
2	PH	DMSO	−0.21	24
3	CH	DMSO	−0.21	25
4	CH	DMSO	−0.31	26
5	CH	DMSO	−0.32	26
6	CH	$MeNO_2$	−0.45	27
7	OH	80% EtOH	−0.59	28
8	OH	7% EtOH	−0.64	28
9	OH	CH_3NO_2	−0.75	29
10	OH	CH_3NO_2	−1.15	29

* The papers from which the data for calculations were taken.

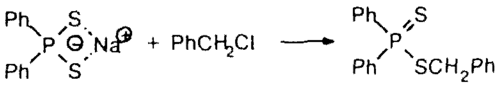
(from +0.08 to −1.15), *i.e.*, the character of the effect of this substituent can vary from more accepting (less donating) to substantially more donating compared to that observed for the standard acid Ph_2POOH. Consideration of the data in Table 1 (their number can be considerably increased) results in the conclusion that the reason for these changes is the changes in the effective positive charge on the phosphorus atom of the phosphoryl group. In the phosphinite or thiophosphinite anions (reactions (1) and (2), Table 1), the effective positive charge on the phosphorus atom in the P=O(S) group (dipole $P^+{-}O^-$) is weakened by the total negative charge of the anion distributed between the phosphorus and oxygen or sulfur atoms. As a result, the phenyl group becomes accepting. As the σ^Φ constant decreases (increasing its negative value), the P=O dipole experiences the effect of the positive charge (or the positive end of the dipole) of the added groups, the positive charge on the phosphorus atom increases, and the phenyl groups become more and more donating. For example, they become pronounced electron donors in reactions (9) and (10).

The ratios considered can be illustrated by the acid-base properties of carbamoyl-substituted phosphinoxides $R_2P(O)CH_2CONEt_2$. Like CH-acids, when they lose a proton, they are transformed into carbanions with a distributed charge. The effective positive charge on the phosphorus atom decreases, and the phenyl group manifests accepting properties: $\sigma^\Phi = -0.31$ (in DMSO). However, when a proton is added to such a phosphinoxide, the effective positive charge on the phosphorus atom increases and, hence, the accepting properties of the phenyl groups decrease, and their donating properties increase. According to the value of σ^Φ of the phenyl group, the protonation of carbamoyl phosphinoxide, which proceeds at the C=O group results in a situation close to standard (the dissociation of the acid Ph_2POOH): $\sigma^\Phi = -0.58$.[19]



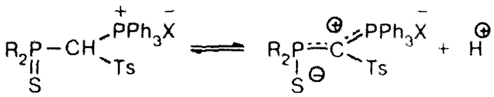


Let us give one more indicative example. For the dissociation of $R_2P(S)SH$ acids in anhydrous EtOH, the constant of the phenyl group (in the Ph_2P fragment) can be calculated as $\sigma^\Phi = -0.55$, *i.e.*, it is close to the standard.[30] In the reaction of the corresponding sodium salt with benzyl chloride (the reaction kinetics was studied)



the σ^Φ constant of the phenyl group becomes equal to −1.25. In the ion pair or in the covalent complex with the sodium ion, the effective positive charge of the phosphorus atom is much higher than the charge on the Ph_2PSS^- anion, and the phenyl group becomes a pronounced donor.[16,17]

It is noteworthy that the σ^Φ constants and, hence, the electronic effects of the phenyl groups, against the assertion of the authors of Ref. 14, are strongly prone to the influence of solvents. Examples for the reactions of acidic dissociation (11)—(14) are presented in Table 2.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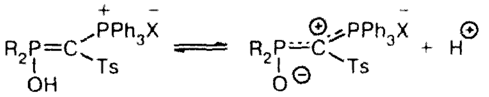
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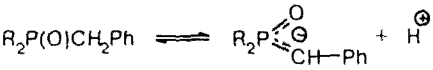
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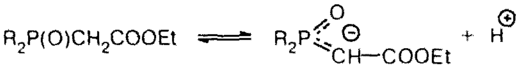

(14)

Table 2. Effect of the solvent on the σ^Φ constant of the phenyl group

Reaction	Acidity	Solvent	σ^Φ	Ref.
11	CH	$MeNO_2$ EtOH	−0.45 −0.46	27
12	OH	$MeNO_2$ EtOH	−1.15 −0.24	29
13	CH	DG* DMSO	−0.58 −0.32	26
14	CH	DG* DMSO	−0.30 −0.22	29

* Diglyme.

For the dissociation of the CH-acid [reaction (11)], the σ^Φ constants in nitromethane and ethanol are equal (−0.45 and −0.46). However, it can be seen that in reaction (12) the OH-acidity of the phosphorane-phosphonium moiety depends strongly on the solvent: σ^Φ changes from −0.24 in alcohol to −1.15 in nitromethane. The more solvating alcohol stabilizes the anionic forms in which, reasonably, the effective positive charge on the phosphorus atom increases and, hence, the donating properties of the phenyls decrease and their accepting properties increase. Many such examples can be presented.

Now let us consider the ratios observed in extraction (Table 3).

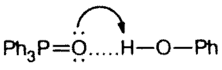
Protonation both of monodentate ($R_3P{=}O$) and bidentate ($R_2P(O)CH_2P(O)R_2$ and $R_2P(O)CH_2CONR_2$) extractants depends, of course, on the nature of the R group, but the phenyl groups are characterized by the σ^Φ constants (−0.58 and −0.59) relative to that of the

Table 3. Constants σ^{Φ} of extractants in various reactions

Extractant	Reaction	Medium	$\sigma^{\Phi}{}_{Ph}$	Ref.
R_3PO	Equilibrium protonation	CH_3NO_2	−0.59	32
$R_2P(O)CH_2P(O)R_2$	Equilibrium protonation	CH_3NO_2	−0.59	1
$R_2P(O)CH_2C(O)NR_2'$	Equilibrium protonation	CH_3NO_2	−0.58	28
$R_2P(O)CH_2C(O)NR_2'$	Extraction of HNO_3	ClC_2H_4Cl	−0.67	34
$R_2P(O)CH_2P(O)R_2$	Extraction of HNO_3	ClC_2H_4Cl	−0.71	35
$R_2P(O)CH_2C(O)NR_2'$	Extraction of Am(III)	ClC_2H_4Cl	−1.17	34
$R_2P(O)CH_2P(O)R_2$	Extraction of Am(III) and Pu(IV)	ClC_2H_4Cl	−1.43	5
R_3PO	Complex formation with HOPh	CCl_4	−0.88	29
R_3PO	Complex formation with HOC_6H_4F-*p*	CCl_4	−0.88	33

standard (dissociation of the acid Ph_2POOH). They are not stronger acceptors and stronger donors than in diphenylphosphinic acid (Ph_2POOH), which is accepted in the given case as the zero point.

For the extraction of nitric acid, the phenyl groups manifest somewhat more donating (less accepting) properties (σ^{Φ} = −0.67, −0.71). We have shown previously that nitric acid forms 1 : 1 and 1 : 2 complexes with diphosphinoxides with strong hydrogen bonds $P{=}O...HNO_3$ (in dichloromethane or chloroform).[31] No elimination of a proton from an HNO_3 molecule occurs. Some increase in the effective positive charge on the phosphorus atom is observed. Unfortunately, dipole moments were not studied for the P=O...H—O system, therefore, it is difficult to make a judgement about charge transfer. However, the formation of complexes by hydrogen bonds has been studied previously.[29,33] For example, in complexes of monophosphinoxides with phenol and *para*-fluorophenol the σ^{Φ} values of the phenyl groups are −0.88, which attests to their increased donor properties: charge transfer occurs in the formation of the complex



$$Ph_3P{=}\ddot{O}.....H{-}O{-}Ph$$

The dipole moment of the system with the H-bond is much greater than that of the initial triarylphosphinoxide (for $Ph_3P{=}O$, −4.1 D, for the complex, 6.5 D). Owing to the charge transfer, the phosphorus atom becomes more positive, and the phenyl groups exhibit pronounced donor properties.[36]

In the case of the formation of complexes between bis-phosphinoxides and Am(III),[5,34] the phenyl groups are characterized by very high negative values of σ^{Φ} (−1.17 and −1.43) and exhibit donor properties. The positive charge on the phosphorus atom caused by the formation of the Am(III) complex is great, due to the transfer of a charge from the phosphoryl group to the metal cation. This explains the "anomalous arylic strengthening." In fact, it is not anomalous. The strong charge transfer in the formation of the strong complex makes the phenyl groups donating, which strengthens the complex more. Thus, phenyl strengthening exists, but only in the cases when a strong complex involving two P=O groups is formed, and the phenyl group, as a "two-faced Janus," appears in its natural donating function.

The absence of noticeable phenyl strengthening in the extraction of Pu(IV), Pu(VI), and U(VI), whose extraction constants (K_{ex}) by bidentate neutral organophosphorus compounds are higher in most cases than K_{ex} of trivalent TPE and REE, does not contradict the aforesaid assertion. The decrease in K_{ex} for these elements in the series $K_{ex}{}^{Oct}$—$K_{ex}{}^{Ph}$ is very small: it is only twofold (instead of 300-fold for the monodentate analogs). Therefore, additional strengthening of the complexes also takes place in this case, but it is disguised by the higher sensitivity of Pu(IV), Pu(VI), and U(VI) to inductive effects.[1,37]

In conclusion, let us consider the effect observed for phosphinoxides $R_2P(O)CH_2CONR_2'$.[14] The authors of Ref. 14 have established that the "phenyl strengthening" depends strongly on the solvent and believe that the electronic effect of the phenyl group cannot depend on the solvent. We have shown above that the σ^{Φ} values of the phenyl groups in fact can strongly depend on the solvent. Unfortunately, the experimental data presented in Ref. 14 are insufficient for calculating the σ^{Φ} constants. However, the latter were estimated for tetrachloroethylene (σ^{Φ} = −1.00), CCl_4 (σ^{Φ} = −1.12), and dichloroethane (σ^{Φ} = −1.17). As can be seen, for weakly polar solvents (tetrachloroethylene, CCl_4), compared to the octyl group (σ^{Φ} = −1.11), the phenyl group in these compounds is an acceptor (a weaker donor), and in dichloroethane, it is explicitly a stronger donor than the octyl group (σ^{Φ} = −1.17). There is no "arylic strengthening" in the first two solvents, while the phenyl effect is observed in dichloroethane (and in the other strongly solvating solvents used in Ref. 14). Of course, the matter is not in the solvation of the extractant, as the authors of Ref. 14 believe, but in the solvation of the complex formed. Efficient solvation increases the stability of the complex, the effective positive charge on the phosphorus atom increases, and the phenyl substituents become donors. Thus, "phenyl strengthening" is subject to the influence of solvents.

It should be said in conclusion that we agree with the opinion[1–5] presented in the beginning of this work concerning the role of the delocalization of the electron density from the aryl groups to the cycle closed by a metal in the strengthening of the complex. At the same time, our experimental material on extraction of actinides, lanthanides, and some other elements, as well as the calculation parameters of the correlation analysis allowed us to look more widely at the problem and, based on the data on the electronic effects of aryl substituents, to formulate ideas about the reasons for the "arylic strengthening" of the extraction capacity of BNOPC, which can be presented as the following statements.

1. Since the phenyl group is biphilic, it can exhibit both donating and accepting properties. When added to a phosphoryl group, it can be a weak electron acceptor, as in dialkyl phosphites, or a fairly strong donor when the phosphonium character of the phosphorus atom increases.

2. The "phenyl strengthening" of complexes with strongly accepting cations actually exists. It depends on the degree of the transfer of a charge from the oxygen atom of the phosphoryl group to the cation-complex-forming agent. There is no "phenyl strengthening" in weak complexes, because their phenyl groups are weak donors (actually they are acceptors). Strong complexes exhibit "phenyl strengthening."

3. There is nothing anomalous in the "phenyl strengthening" of complexes with electron-accepting cations.

4. There is a dependence of the "phenyl strengthening" effect on the solvent: the effect increases in strongly solvating solvents, which stabilize the complex, and decreases or disappears in weakly solvating solvents.

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