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Microwave-assisted synthesis of dialkylphosphinic acids and a structure–reactivity study in rare earth metal extraction†

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Dialkylphosphinic acids were synthesised by a microwave-assisted method with high yields and wide substrate applicability. A structure–reactivity study indicates that an increase in steric hindrance in the β position led to a decrease of extraction ratio and heavy rare earth element separation activity. A computational study was also conducted to understand the steric effect.

Increasing demands for rare earth elements in industry has led to an increasing interest in rare earth separation and purification in recent years.[1] Rare earth separation has been carried out mostly using phosphonate acids, such as 2-ethylhexylphosphonic acid mono-2-ethyl-hexyl ester (P507, PC88).[2–6] However, high concentration stripping acids and low separation efficiency hinder the separation of heavy rare earths in the P507 separation system.[7,8] With the increasing requirements of environmental protection and demands for rare earths, it is necessary to find a more efficient rare earth extractants to solve these problems. Phosphinic acids are a series of extractants may possibly solve the stripping acidity and separation efficiency at one time. When carbon–phosphorus bonds replace oxygen–phosphorus bonds, dialkylphosphinic acid demonstrated higher pK_a values than phosphonic acids and phosphoric acids.[9–11] So the stripping acidity could be decreased obviously using dialkylphosphinic acid in rare earth extraction. However, previous studies showed some discrepancies about the effect of steric hindrance on the separation efficiency of rare earths.[12–14] Nagaosa *et al.* summarized that large steric hindrance would lead to a decrease in overall selectivity in rare earth separation,[12] especially in the extraction of heavy rare earth metals. In contrast, Yuan's studies indicated that steric hindrance usually provides a higher selectivity in rare earth extraction, especially for light rare earths with a larger ionic radius.[13] Pánková's research illustrated that the selectivity does not depend much on the structure or size of the alkyl substituent, but is influenced considerably by the branching extent of the alkyl group.[14] Therefore, the influence of the steric hindrance in dialkylphosphinic acids on the extraction remains to be further investigated.

Unfortunately, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) is the only commercially available phosphinic acid extractant.[15–17] A major reason is that the synthetic methods for dialkylphosphinic acids are usually inconvenient and poorly efficient. Grignard reaction and free-radical addition are often used to prepare the dialkylphosphinic acids.[18–21] The Grignard reaction requires three steps, harsh reaction conditions and often suffers from low yield, which restricted its application.[13,18] High pressure and long reaction time often make the free-radical addition inconvenient and low efficient.[19–21] Therefore, an improved method for the synthesis of phosphinic acids should be developed, then the structure–reactivity study could be possibly done and more efficient extractant could be developed therein.

Considering the high efficiency of microwaves (MWs) in organic synthesis,[22–24] we employed it in the preparation of phosphinic acids with different substituents at the β-position. Steric hindrance in the β-position was studied and structure–reactivity was investigated and further explained by theoretical calculation.

Under MW irradiation, the influence of solvent, initiator and temperature on the reaction was first investigated, as shown in Table 1. Azodiisobutyronitrile (AIBN), benzoperoxide (BPO), *tert*-butyl hydroperoxide (*t*-BuOOH) and di-*tert*-butyl peroxide (DTBP) were added as initiators. As reported by Li, DTBP exhibits a high initiation efficiency,[19] with only 0.2 equivalent of DTBP to provide excellent yields (Table 1, entries 1–4). Only 2 h were required for the completion of the reaction. DMF was found to be a suitable solvent compared with AcOH and DME (Table 1, entries 7–9).

Different α-olefins were tested for their suitability under the above MW-assisted reaction conditions. It was found that

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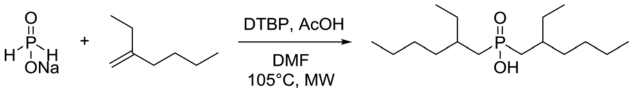
Table 1 Optimization of reaction conditions



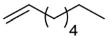
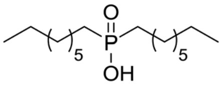
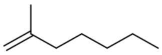
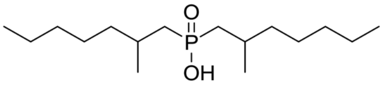
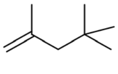
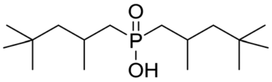
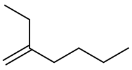
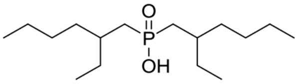
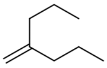
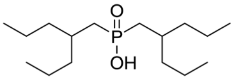
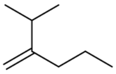
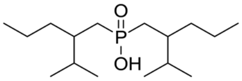
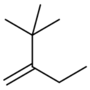
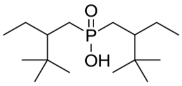
Entry	Initiator (equiv.)	Solvent	Time (h)	Yield[a] (%) DPA : HPA : SHP
1	DTBP (0.2)	DMF	2	95 : 4 : 1
2	AIBN (0.2)	DMF	2	0 : 63 : 37
3	BPO (0.2)	DMF	2	2 : 45 : 53
4	*t*-BuOOH (0.2)	DMF	2	9 : 47 : 44
5	DTBP (0.2)[b]	DMF	8	95 : 4 : 1
6	DTBP (0.2)	DMF	4	96 : 3 : 1
7	DTBP (0.2)	AcOH	2	82 : 17 : 1
8	DTBP (0.2)	Dioxane	2	56 : 33 : 11
9	DTBP (0.2)	DME	2	14 : 11 : 75

[a] Dialkylphosphinic acid (DPA) : H-phosphinic acid (HPA) : sodium hypophosphite (SHP); ^{31}P NMR yields. [b] DTBP (0.2 equiv.) was added twice.

moderate to excellent yields of disubstituted phosphinic acids can be obtained in most cases (Table 2 and ESI†). The *n*-octylene, 2-methylheptylene, 2-ethylhexylene and 2-propylpentene give yields more than 82% (Table 2, entries 1, 2, 4 and 5). But 2-isopropylpentene and 2-*t*-butylbutene gave lower yields (Table 2, entries 6–7), largely owing to the steric effect of isopropyl and *t*-butyl in the β position. Though the diisobutylene composed of 80% α-type and 20% β-type olefin decreases the yield from 82% to 79%, it is higher than 64.3% and 75.3% reported by Li and Wo respectively (Table 2, entries 3).[19–21] Meanwhile, there are only 2 h needed to complete the reaction comparing 30 h and 45 h reported by Li and Wo.

As shown in Table 2 (entries 1–7), the spatial structure of substituents can have a significant effect on their pK_a values. pK_a values of compounds increase gradually from 4.96 to 6.05 as P208 < P218 < Cyanex272 < P227 < P236 < P2361 < P247, which is consistent with the increase of steric hindrance in β position as H < methyl < ethyl < propyl < isopropyl < *t*-butyl.

Table 2 Scope of synthesis of disubstituted phosphinic acids

Entry	Olefin	Phosphinic acid	Yield[a] (%)	pK_a	Remark
1			91	4.96	P208
2			86	5.42	P218
3			83(79[b])	5.58	P272
4			92	5.61	P227
5			84	5.71	P236
6			70	5.80	P2361
7			70	6.05	P247

[a] Yield of isolated product. [b] The feed olefin was diisobutylene composed 80% α-type and 20% β-type.

The performance of rare earth extraction with these dialkylphosphinic acids was then explored. The extraction of Ln^{3+} from the aqueous phase was studied for Ln (0.01 M), HL (0.2 M), (Na, H)Cl (1 M) and pH = 3. Dialkylphosphinic acid exists as a dimer in aliphatic solvent. Hence, the dialkylphosphinic acid extractant can be considered to occur as $(HL)_2$ in rare earth extraction. The equilibrium with dialkylphosphinic acid can be represented as follows:

$$Ln^{3+}{}_{(a)} + 3(HL)_{2(o)} \rightleftharpoons [Ln(HL_2)_3]_{(o)} + 3H^{+}{}_{(a)} \tag{1}$$

In this equation, subscripts a and o denote species in the aqueous and organic phases, respectively. The extraction concentration equilibrium constant, K_{ex}, is given by:

$$K_{ex} = \frac{[Ln(HL_2)_3]_{(o)}[H^+]^3{}_{(a)}}{[Ln^{3+}]_{(a)}[(HL)_2]^3{}_{(o)}} = \frac{D[H^+]^3{}_{(a)}}{[(HL)_2]^3{}_{(o)}} \tag{2}$$

where the distribution ratio D of the lanthanide is given by $D = [Ln(HL_2)_3]_{(o)}/[Ln^{3+}]_{(a)}$.

As shown in Fig. 1 and Table 3, in general, K_{ex} for La, Pr, Nd, Dy, Ho, Yb and Lu extraction decrease as P218 > P208 > Cyanex272 > P227 > P236 > P2361 > P247, except for La. Because the solubility of P208 is poor in *n*-dodecane, toluene was selected as the solvent to explore the extraction ability. K_{ex} for rare earth extraction with dialkylphosphinic acid in *n*-dodecane is greater than that in toluene (Table S3†). Therefore, the difference in extraction ratios could be explained for pK_a values (Table 2, entries 1–7). The pK_a increased as $4.96 < 5.42 < 5.58 < 5.61 < 5.71 < 5.80 < 6.05$ with increasing in steric hindrance, whereas the K_{ex} decreased.

As shown in Table 3, the separation factor $\beta_{Nd/La}$ is in same order of magnitude where $\beta_{Lu/Dy}$ differ from an order of magnitude or more. Similar $\beta_{Nd/La}$ indicate that there is not much difference in light rare earth separation by various dialkylphosphinic acids. Therefore, the substituent in the β-position of dialkylphosphinic acids has few influence on the light rare earths separation. A possible reason is that light rare earths have larger ionic radius. However, the $\beta_{Lu/Dy}$ of P227 is an order of magnitude higher than $\beta_{Lu/Dy}$ of P247 and P2361. The difference of $\beta_{Lu/Dy}$ for various dialkylphosphinic acids in the extraction of heavy rare earth is closely related to the steric hindrance of extractants. The increase in steric hindrance of the alkyl chain leads to a decrease in separation efficiency in heavy rare earth separation. Furthermore, the influence of branching of the alkyl group can be found in Table 3 (entries 3 and 7). There are little differences exist between methyl and ethyl in steric hindrance between P247 and P272, but the K_{ex} of P272 in the extraction equilibrium are of a 1 to 2 orders of magnitude higher than those of P247 (Table 3, entries 3 and 7). This result demonstrates that the effect of steric hindrance is greater than that from branching of the alkyl group. It should be mentioned that P272 which branched on the terminal carbon has good separation efficiency, but the terminal branched group also leads to a decrease in saturation capacity.[7,8] In summary, steric hindrance is important for rare earth metal separation, especially for heavy rare earths separation. The results revealed that ethyl and propyl substituents in the β-position of dialkylphosphinic acids are most suitable for rare earth separation.

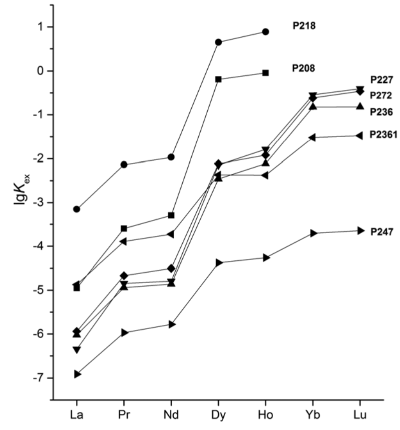


Fig. 1 Extraction equilibrium constants of rare earth metal extraction by dioctylphosphinic acid.

A computational study was conducted to understand the steric effect on extraction equilibrium. As Garcés *et al.* reported,[25] the difference between a stepwise and intrinsic stability constant would be constant or vary systematically with changes for multiple coordinate complexes. Based on this approximation, the following equation has been proposed to represent the extraction reaction from aqueous to organic phase:

$$\begin{aligned}1/2H_2L_{2(o)} + [M(H_2O)_9]^{3+}{}_{(a)} + 3H_2O_{(a)} \\ \rightarrow [M(H_2O)_8L]^{2+}{}_{(o)} + H_9O_4{}^{+}{}_{(a)}\end{aligned} \tag{3}$$

The formations of reactants and products were found from the work by Clark, Yang and Yuan respectively.[20,26,27] The computational results are listed in Table 4.

Table 4 shows that ΔG_{Lu} is always more negative than ΔG_{La} both in vacuum and in solvent for all extractants. This computational result agrees well with experimental result that the extraction of Lu has higher K_{ex} than that of La. For the same metal, the K_{ex} is influenced by substituents in the β-position. For example, the order of ΔG_{Lu} is P208 < P272 ≈ P227 < P236 < P218 < P2361 < P247 with the substituent in β position changed by the order H < metyl < ethyl < propyl < isopropyl < *t*-butyl, which agrees with the experimental K_{ex}, except for P218. Finally, the difference between ΔG_{Lu} and ΔG_{La} could be used to evaluate extractant separation activity. For instance, the absolute value of $\Delta G_{Lu} - \Delta G_{La}$ for P247 is smaller than that for P227, and its separation activity is poorer. The order of separation activity for rare earths from computational results is P236 > P227 > P272 > P2361 > P247, which agrees with experimental results, except for P236. Consequently, the effect of steric hindrance in the β-position can be evaluated conveniently through proper approximation.

In conclusion, dialkylphosphinic acid was synthesized by optimized MW-assisted free radical addition. The reaction gives higher yields and completed in only 2 h comparing 30 h or more in traditional method. Moreover, this strategy has good

Table 3 Extraction ratio and extraction equilibrium constants for rare earth metal extraction by dioctylphosphinic acid (%)

Entry	Extractant[a]	β-Substituent		La	Pr	Nd	Dy	Ho	Yb	Lu	$\beta_{Nd/La}$	$\beta_{Lu/Dy}$
1	P208	None	E (%)	17.45	38.72	47.35	98.97	99.06	100	100	45.50	—
			K_{ex}	1.11×10^{-5}	2.53×10^{-4}	5.05×10^{-4}	0.65	0.91	—	—		
2	P218	Methyl	E (%)	47.52	65.41	73.20	99.65	99.78	100	100	14.31	—
			K_{ex}	6.99×10^{-4}	7.32×10^{-3}	0.01	4.5	7.83	—	—		
3	P272	Methyl	E (%)	7.88	17.46	19.24	65.64	75.97	96.22	97.67	14.53	43.60
			K_{ex}	9.50×10^{-7}	1.15×10^{-5}	1.38×10^{-5}	3.44×10^{-3}	7.68×10^{-3}	0.14	0.15		
4	P227	Ethyl	E (%)	6.86	16.47	17.3	66.81	73.16	95.57	96.6	35.62	54.78
			K_{ex}	4.52×10^{-7}	1.42×10^{-5}	1.61×10^{-5}	7.12×10^{-3}	1.61×10^{-2}	0.30	0.39		
5	P236	Propyl	E (%)	8.93	22.17	19.69	62.32	68.66	94.48	95.58	27.30	44.62
			K_{ex}	1.15×10^{-6}	2.15×10^{-5}	3.14×10^{-5}	7.62×10^{-3}	1.19×10^{-2}	0.24	0.34		
6	P2361	Isopropyl	E (%)	15.62	27.88	28.86	53.99	58.31	77.83	77.52	13.93	7.87
			K_{ex}	1.35×10^{-5}	1.28×10^{-5}	1.88×10^{-4}	4.22×10^{-3}	4.16×10^{-3}	3.03×10^{-2}	3.32×10^{-2}		
7	P247	*t*-Butyl	E (%)	10.42	15.05	13.77	25.4	27.72	41.16	36.97	13.61	5.41
			K_{ex}	1.22×10^{-7}	1.07×10^{-6}	1.66×10^{-6}	4.18×10^{-5}	5.45×10^{-5}	1.97×10^{-4}	2.26×10^{-4}		

[a] Extraction condition: 0.2 M extractants in *n*-dodecane (P208 was in toluene), $[LnCl_3] = 0.01$ M, ion strength: 1 M (Na, H)Cl, initial pH = 3, phase ratio: 1 : 1.

Table 4 Free energy of proposed extraction reaction (kJ mol^{-1})

	In vacuum			In solvent		
Extractant	ΔG_{La}	ΔG_{Lu}	$\Delta G_{Lu} - \Delta G_{La}$	ΔG_{La}	ΔG_{Lu}	$\Delta G_{Lu} - \Delta G_{La}$
P208	−605.35	−644.52	−39.17	−24.15	−85.34	−61.19
P218	−605.32	−638.46	−33.14	−24.89	−73.85	−48.96
P272	−599.12	−639.17	−40.05	−15.61	−75.97	−60.36
P227	−595.95	−640.95	−45.00	−13.18	−75.50	−62.32
P236	−595.04	−640.47	−45.43	−10.34	−74.23	−63.89
P2361	−597.53	−634.32	−36.80	−12.16	−68.80	−56.64
P247	−600.97	−639.38	−38.41	−19.25	−65.85	−46.61

substrate adaptability by using different α-olefins. 7 phosphinic acids were synthesized, of which P218, P236, P2361 and P247 were synthesized for the first time. The structure–reactivity study by experiment and computation indicated steric effect in the β-position influence separation efficiency evidently. Ethyl or propyl substituents in β-position give higher separation activity in rare earths extraction. Higher or lower steric hindrance in β-position will decrease the separation efficiency. The effect of substituent in β-position can be evaluated conveniently through a simplified model by computational study. This research will be useful for designing new rare earth metal extractants.

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