Minimizing Solvent Waste in Catalytic Reactions in Highly Recyclable Hydrocarbon Solvents

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General procedure for determining the percent leaching of PAO and heptane into the polar solvents by ¹H NMR analysis¹

PAO (10 mL) or heptane (10 mL) were weighed and mixed with CH₃CN (3 mL) in a centrifuge tube and the total weight determined. The biphasic mixture was vortexed (3000 rpm) for 2 min at ambient temperature and centrifuged (3000 rpm, 30 min). Then a sample of the CH₃CN (100 mg) was removed by pipet, transferred to an NMR tube, and dissolved in CDCl₃ for ¹H NMR spectroscopic analysis. The ¹H NMR spectra were perforned at ambient temperature with a number of scans of 64 and an acquistion time of 4 s for each spectrum. This experiment was performed at least 2 times and the results averaged.

To determinate the amount of PAO in the polar phase, the integral of CH₃CN peak at 1.94 ppm was set to 100. The integrals of the two ¹³C satellite peaks of the CH₃CN were assembled and combined. Then the combined integrals of the signals from the PAO or the heptane region (0.8 - 1.2 ppm) were recorded. Finally, we calculated the amount of PAO (mg) in the CH₃CN phase and compared with the amount of the original PAO (10 mL). The calculation the amount of PAO in CH₃CN based on the number of protons of CH₃CN (3 H) and PAO (74 H) or heptane (16 H), the molecular weight of the compounds, and the amount in each phase, relied on the 1.1% natural abundance of ¹³C in CH₃CN as shown below.

In order to demonstrate the percent leaching of PAO or heptane containg 2M toluene as a cosolvent, PAO (8 mL) or heptane (8 mL) were weighed and mixed with toluene (2 mL) in a centrifuge tube. Then the polar solvent (3 mL) including CH₃CN, H₂O/CH₃CN (5% v/v) and H₂O/CH₃CN (10% v/v) was added and carried out the experiments in the same fashion.

PAO leaching calculation



Heptane leaching calculation

$$\underbrace{ \begin{array}{c} \text{integral of PAO} \\ 0.8-1.2 \text{ ppm} \\ \text{integral of CH}_3\text{CN} \\ \text{integral of CH}_3\text{CN} \\ \text{satellite peaks} \end{array}} \left(\begin{array}{c} 3 \text{ H in} \\ \frac{13}{\text{CH}_3\text{CN}} \\ 1 \text{ mole of} \\ \frac{13}{\text{CH}_3\text{CN}} \\ 43 \text{ g of} \\ \frac{13}{\text{CH}_3\text{CN}} \\ 13 \text{ G} \\ 13 \text{CH}_3\text{CN} \end{array}} \right) \left(\begin{array}{c} 0.011 \text{ g of} \\ \frac{13}{\text{CH}_3\text{CN}} \\ 1 \text{ g of} \\ 13 \text{CH}_3\text{CN} \end{array} \right) \left(\begin{array}{c} 1 \text{ mole of} \\ \frac{13}{\text{CH}_3\text{CN}} \\ 1 \text{ g of} \\ 13 \text{CH}_3\text{CN} \end{array} \right) \left(\begin{array}{c} 1 \text{ mole of} \\ \frac{16 \text{ H in}}{16 \text{ petane}} \\ 16 \text{ heptane} \end{array} \right) \left(\begin{array}{c} 100 \text{ g of} \\ \frac{16 \text{ mole of}}{16 \text{ mole of}} \\ \frac{16 \text{ mole of}}{16 \text{ petane}} \end{array} \right) \left(\begin{array}{c} 1 \text{ mole of} \\ \frac{16 \text{ mole of}}{16 \text{ mole of}} \\ \frac{16 \text{$$

Sample PAO leaching calculation

$$\begin{pmatrix} 0.062 \text{ H of PAO} \\ 0.8-1.2 \text{ ppm} \\ \hline 0.96 \text{ H of CH}_3\text{CN} \\ \text{satellite peaks} \end{pmatrix} \begin{pmatrix} 3 \text{ H in} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \begin{pmatrix} 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{43 \text{ g of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1^3\text{CH}_3\text{CN}} \end{pmatrix} \begin{pmatrix} \hline 0.011 \text{ g of} \\ \frac{1^3\text{CH}_3\text{CN}}{43 \text{ g of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1^3\text{CH}_3\text{CN}} \end{pmatrix} \begin{pmatrix} \hline 0.011 \text{ g of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ g of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1^3\text{CH}_3\text{CN}} \end{pmatrix} \begin{pmatrix} \hline 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \begin{pmatrix} \hline 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \begin{pmatrix} \hline 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \begin{pmatrix} \hline 2.16 \text{ g of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \begin{pmatrix} 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \begin{pmatrix} 1 \text{ mole of} \\ \frac{1^3\text{CH}_3\text{CN}}{1 \text{ mole of}} \end{pmatrix} \end{pmatrix}$$

Sample heptane leaching calculation

10.4 H of PAO 0.8-1.2 ppm 0.10 H of CH ₃ CN satellite peaks	$\begin{pmatrix} 3 \text{ H in} \\ \frac{^{13}\text{CH}_3\text{CN}}{1 \text{ mole of}} \\ ^{13}\text{CH}_3\text{CN} \end{pmatrix}$	$ \begin{pmatrix} 1 \text{ mole of} \\ \frac{^{13}\text{CH}_3\text{CN}}{43 \text{ g of}} \\ ^{^{13}\text{CH}_3\text{CN}} \end{pmatrix} $	$ \begin{array}{r} \hline 0.011 \text{ g of} \\ \frac{1^{3}\text{CH}_{3}\text{CN}}{1 \text{ g of}} \\ 1^{3}\text{CH}_{2}\text{CN} \end{array} $	1 mole of heptane 16 H in heptane	100 g of heptane 1 mole of heptane	$\begin{pmatrix} 2.24 \text{ g of} \\ CH_3CN \end{pmatrix}$	=	0.12 g of heptane 6.76 g of original heptane	× 100
			′Ҷ¹℃H₃CNノ		Cicpianc	/		onginal neptane	

Table S1. ¹H NMR spectroscopic analysis of PAO or heptane leaching into polar phases

Non polar Entries		Polar phase	PAO or he polar phase (mg	ptane in) from ¹ H NMR	original PAC mass	leaching (%)	
	phase		1 st	2 nd	1 st	2 nd	average
1	PAO	CH₃CN	0.7	0.7	8208	8191	0.01
2	heptane	CH₃CN	115	102	6763	6782	1.60
3	2 M toluene	CH₃CN	4.0	4.2	6494	6614	0.06
4	in PAO	5% H ₂ O:CH ₃ CN	1.8	1.8	6508	6627	0.03
5		10% H ₂ O:CH ₃ CN	1.6	1.4	6405	6630	0.02
6	2 M toluene	CH₃CN	312	303	5403	5413	5.7
7	in heptane	5% H ₂ O:CH ₃ CN	139	148	5350	5479	2.7
8		10% H ₂ O:CH ₃ CN	69	65	5338	54372	1.2

¹H NMR spectra of PAO and heptane leaching into polar phases



Figure S1.¹H NMR spectrum of PAO leaching into CH₃CN phase in CDCl₃



Figure S2.¹H NMR spectrum of heptane leaching into CH₃CN phase in CDCl₃



Figure S3. ¹H NMR spectrum of PAO containing toluene leaching into CH₃CN phase in CDCl₃



Figure S4.¹H NMR spectrum of heptane containing toluene leaching into CH₃CN phase in CDCl₃



Figure S5.¹H NMR spectrum of PAO containing toluene leaching into H₂O/MeCN (5% v/v) in CDCl₃



Figure S6. ^1H NMR spectrum of heptane containing toluene leaching into H_2O/MeCN (5% v/v) in CDCl_3



Figure S7.¹H NMR spectrum of PAO containing toluene leaching into H₂O/MeCN (10% v/v) in CDCl₃



Figure S8. 1H NMR spectrum of heptane containing toluene leaching into H_2O/MeCN (10% v/v) in CDCl_3

General procedure for studying solvent effects on the rate of Boc-protection of 2,6-

dimethylphenol



The rate of Boc-protection of 2,6-dimethylphenol was measured in various solvents such as heptane, PAO₅₀₆, 5 M toluene and 5 M THF in PAO₅₀₆, toluene, and THF. These studies were carried out at 0 °C and used 0.5 mol% **5** as a catalyst with 0.2 M 2,6-dimethylphenol and 0.24 M (Boc)₂O. Due to the fact that two substrates were slightly different in concentration, the pseudo first-order plots of disappearance ln[2,6-dimethylphenol] versus time were only measured for the first 30-40% conversion to provide the rate constants. These rate plots are shown in Figure S1.



Figure S9. Kinetic plots of Boc-protected 2,6-dimethylphenol in heptane, PAO, PAO solvent mixtures, toluene, and THF

¹H and ¹³C NMR spectra of polyisobutylene derivatives



Figure S10.¹H NMR spectrum of hydroxy-terminated PIB oligomer (1)



Figure S11.¹³C NMR spectrum of hydroxy-terminated PIB oligomer (1)



Figure S12. ¹H NMR spectrum of iodo-terminated PIB oligomer (2)



Figure S13. ¹³C NMR spectrum of iodo-terminated PIB oligomer (2)



Figure S14. ¹H NMR spectrum of Boc-piperazine-terminated PIB oligomer (3)



Figure S15. ¹³C NMR spectrum of BOC-piperazine-terminated PIB oligomer (3)



Figure S16. ¹H NMR spectrum of piperazine-terminated PIB oligomer (4)



Figure S17. ¹³C NMR spectrum of piperazine-terminated PIB oligomer (4)



Figure S18. ¹H NMR spectrum of DMAP-terminated PIB oligomer (5)



Figure S19. ¹³C NMR spectrum of DMAP-terminated PIB oligomer (5)



¹H and ¹³C NMR spectra of product from catalytic reactions using catalyst 5

Figure S20. ¹H NMR spectrum of Boc-protected 2,6-dimethyl phenol



Figure S21. ¹³C NMR spectrum of Boc-protected 2,6-dimethyl phenol



Figure S22. ¹H NMR spectrum of menthyl acetate



Figure S23. ¹³C NMR spectrum of menthyl acetate



Figure S24. ¹H NMR spectrum of 2-phenyl-2-((trimethylsilyl)oxy) acetonitrile



Figure S25. ¹³C NMR spectrum of 2-phenyl-2-((trimethylsilyl)oxy) acetonitrile



Figure S26. ¹H NMR spectrum of ethyl-(*E*)-3-(4-chlorophenyl)-2-cyanoacrylate



Figure S27. ¹³C NMR spectrum of ethyl-(*E*)-3-(4-chlorophenyl)-2-cyanoacrylate

References

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