J. Org. Chem. **2000,** *65,* 3107−3110 **3107**

Tandem One-Pot Palladium-Catalyzed Reductive and Oxidative Coupling of Benzene and Chlorobenzene

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Received December 6, 1999

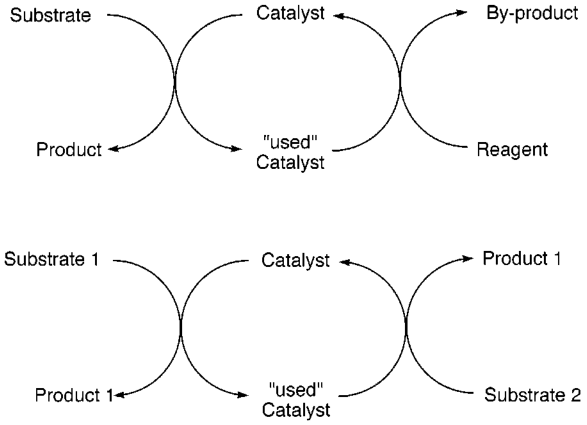
The in situ combination of oxidative coupling of benzene to biphenyl and reductive coupling of chlorobenzene (also to biphenyl) using palladium catalysts (Pd^{2+}/Pd^0) is described. In each cycle, the reductive process regenerates the catalyst for the oxidative process and vice versa. Kinetic investigations show that the reaction rate depends on $[C_6H_6]$, $[C_6H_6Cl]$, and catalyst loading, with $E_a = 13$ kcal mol^{-1}. The reduced palladium catalyst undergoes deactivation through aggregation and precipitation, but it is observed that during this deactivation process the Pd^0 becomes an active catalyst for the reductive coupling of chlorobenzene. Accordingly, while Pd^0/C particles are inactive, Pd^0 colloids do catalyze the tandem reaction. Conversion is increased in the presence of a phase-transfer catalyst, presumably due to stabilization of the active Pd^0 clusters. The two halves of the catalytic cycle are examined in the light of previous research, regarding analogous oxidative and reductive coupling reactions, using stoichiometric amounts of $PdCl_2$ and Pd^0, respectively. The roles of homogeneous $PdCl_2$ and Pd^0 clusters are discussed.

Introduction

Sustainable chemistry and waste effluent minimization feature prominently on the chemists' agenda.[1] The substitution of polluting processes that require stoichiometric amounts of metallic reagents with catalytic reactions may be viewed as the first step toward total eco-efficiency.[2] Unfortunately, ideal, 100% atom-efficient transformations, e.g., the hydrogenation of benzene to cyclohexane,[3a] are usually limited to simple addition or substitution reactions. In some other cases, e.g., replacement of stoichiometric CrO_3 oxidations with Cr-catalyzed oxidation using air or hydrogen peroxide,[3b] in situ catalyst regeneration is relatively simple, but frequently catalyst regeneration leads to additional byproducts and/or waste streams (Scheme 1, top).

Advancing one step further, the ideal catalytic process would involve regeneration of the catalyst using not a reagent, but rather another, different, substrate molecule (Scheme 1, bottom); this second substrate would interact with the "used catalyst", to give the same product as the first, and a recycled catalyst.

Scheme 1



Obviously, one of the likely systems that this concept could be applied to is a circular oxidation−reduction process. In this study, we examine the application of this concept to aryl-aryl coupling reactions, which are of accountable interest in several branches of the chemical industry.[4] The Ullmann[5] (homocoupling) and Suzuki[6] (cross-coupling) reactions are well-known in this context. Intensive research over the past decade has led to the proposal of numerous reductive[7] and oxidative[8] palladium-catalyzed coupling protocols, the common factor of which is the use of the $Pd^{2+} \Leftrightarrow Pd^0$ redox cycle.[9] During our recent investigations into the mechanisms of pal-

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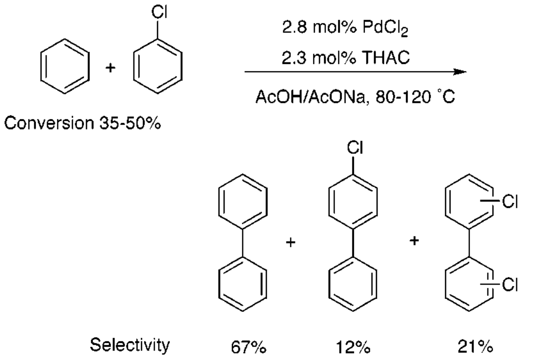
10.1021/jo991868e CCC: $19.00

ladium-catalyzed aryl−aryl coupling,[10,11] we became interested in combining these two pathways in such a concerted manner, so that the starting material for the oxidative coupling would act as the in situ catalyst regenerator in the reductive coupling and vice versa.

Here, we present the application of the above concept to a redox catalytic cycle, namely the tandem oxidative coupling of benzene to biphenyl, with in situ reductive coupling of chlorobenzene, also to biphenyl, and discuss possible mechanisms for this palladium-catalyzed "Ullman-type" reaction.

Results and Discussion

In a typical reaction (eq 1), a 1:1 equivalent mixture of benzene and chlorobenzene together with catalytic amounts of tetrahexylammonium chloride (THAC) and $PdCl_2$ was stirred in an AcOH/AcONa solvent medium in an autoclave at 105 °C for 28 h. Biphenyl was found to be the major product, together with some dichlorobiphenyl and some of the cross-coupling product, 4-chlorobiphenyl. The effects of various reaction parameters on the conversion and selectivity are shown in Table 1. No reaction was observed in the absence of benzene, and only traces of biphenyl (<1%) were observed in the absence of chlorobenzene. Moreover, no reaction was observed when $Pd(OAc)_2$ was used as a catalyst instead of $PdCl_2$, indicating that Cl^- ligands do not exchange readily. When using $PdCl_2$ as catalyst, the reaction ceased after ca. 40% conversion of benzene, due to catalyst deactivation. The deactivated catalyst precipitated as palladium metal particles and could easily be separated from the reaction mixture by filtration.



(1)

Kinetic studies showed the reaction rate to be a function of benzene concentration, chlorobenzene concentration, and catalyst loading, i.e., $-d[C_6H_6]/dt = k[C_6H_6][C_6H_5Cl][PdCl_2]$, wherein first-order dependence was observed for all three variables. A pseudo first-order rate law, $-d[C_6H_6]/dt = k_{obs}[C_6H_6]$, was observed for fixed catalyst loading and chlorobenzene concentrations, with a typical k value of 4×10^{-6} s^{-1}. (To ensure that the rates were not mass transfer controlled, agitation speed was varied from 200 to 950 rpm. Above 800 rpm, no increase in conversion was detected. Thus, all measurements pertain to 950 rpm stirring.) As could be expected, performing the reaction at higher temperatures increased the overall reaction rate. The experimental Arrhenius energy of activation was found to be $E_a = 55$ kJ mol^{-1} (13 kcal mol^{-1}, $r^2 = 0.997$ for four measurements at 75, 85, 95, and 105 °C). When the temperature was raised to 115 °C, however, the rate slowed, which may be attributed to formation of a large quantity of benzene vapor that does not participate in the liquid-phase reaction.

Table 1. Effect of Process Parameters on Benzene Conversion and Selectivity[a]

entry	parameter changed	benzene conv %	biphenyl sel. %[b]
	$PdCl_2$ (M)		
1	0.0175	14	66
2	0.035	23	67
3	0.07	39	67
4	0.14	45	66
	NaOAc (M)		
5	0.0	0	0
6	1.5	15	65
7	2.0	21	67
8	2.5	39	67
9	3.0	39	65
	THAC (g)		
10	0.0	20	69
11	0.2	23	65
12	0.5	31	66
13	1.0	45	67
14	1.2	43	69
	Solvent		
16	AcOH	39	67
17	DMSO	4	62
18	H_2O	0	0
	Catalyst (2.8 mol %)		
19	$PdCl_2$	39	67
20	Pd^0/C	0	<1
21	Pd^0 colloid	13	63

[a] Standard reaction conditions: benzene, 7.8 g (100 mmol); chlorobenzene, 11.3 g (100 mmol); AcONa 13.6 g (100 mmol); $PdCl_2$, 0.5 g (2.8 mol %); THAC, 1.0 g (2.3 mol %); 105 °C; AcOH (total reaction volume), 40 ml, 28 h. [b] Based on GC area, corrected by the presence of an internal standard.

The above system comprises four distinct transformations, three of which make up the oxidative coupling pathway (eqs 2−4), and one, the reductive coupling of C_6H_5Cl, which allows catalyst recycling (eq 5). As we showed earlier, it is impossible to obtain the cross-coupling product via the reductive coupling route.[10a] The complexity of the system is increased by the fact that the homogeneous Pd^0 itself undergoes deactivation through aggregation and precipitation. In addition, the reductive coupling depends on heterogeneous catalysis. To simplify matters, we shall consider the oxidation and reduction reactions separately.

Pd-Catalyzed Oxidative Coupling of Benzenes. It is worthwhile to examine this half of the catalytic cycle on the basis of the oxidative coupling of benzenes with *stoichiometric* amounts of $PdCl_2$ in a similar medium, namely $2C_6H_6 + PdCl_2 + 2NaOAc \rightarrow C_6H_5{-}C_6H_5 + Pd^0 + 2NaCl + 2AcOH$. This reaction was thoroughly investigated by VanHelden et al.,[12] who suggested the following four-step mechanism: (i) reaction between C_6H_6 and $PdCl_2$, arising from $\pi-\sigma$ interactions;[13] (ii) fast reaction

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(9) For an excellent recent monograph on palladium catalysis, see: Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1993.

(10) (a) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Wiener, H.; Sasson, Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2481. (b) Mukhopadhyay, S.; Rothenberg, G.; Wiener, H.; Sasson, Y. *Tetrahedron* **1999**, *55*, 14763.

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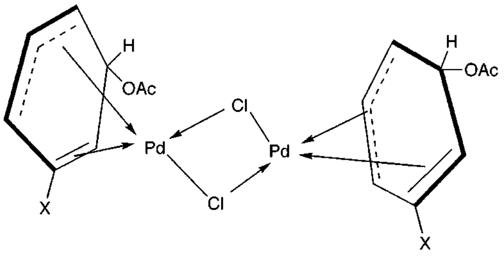
of the $[C_6H_6]^+[PdCl_2]^-$ ion pair with an acetate ion; (iii) dimerization to form complex **1** [analogous to the $(\pi\text{-allyl PdCl}_2)_2$ complex];[14] and (iv) disproportionation of **1** to give the coupling product, Pd^0, and $PdCl_2$. Step (i) was assumed to be rate-determining. The two remaining oxidative couplings (eqs 3 and 4) can be envisaged in a similar manner. Note that the requirement for stoichiometric amounts of $PdCl_2$ stems from the fact that the reduced Pd^0 species precipitates, and cannot be recycled. We found, however, that during this deactivation process the Pd^0 species goes through an intermediate state in which it can catalyze the reductive coupling of C_6H_5Cl, and regenerate as $PdCl_2$.



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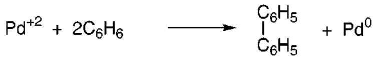
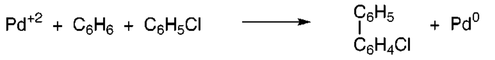
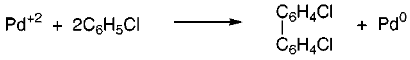


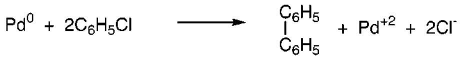
$$\mathrm{Pd^{+2}} + 2\mathrm{C_6H_6} \longrightarrow \begin{array}{c}\mathrm{C_6H_5}\\ | \\ \mathrm{C_6H_5}\end{array} + \mathrm{Pd^0} \qquad (2)$$



$$\mathrm{Pd^{+2}} + \mathrm{C_6H_6} + \mathrm{C_6H_5Cl} \longrightarrow \begin{array}{c}\mathrm{C_6H_5}\\ | \\ \mathrm{C_6H_4Cl}\end{array} + \mathrm{Pd^0} \qquad (3)$$



$$\mathrm{Pd^{+2}} + 2\mathrm{C_6H_5Cl} \longrightarrow \begin{array}{c}\mathrm{C_6H_4Cl}\\ | \\ \mathrm{C_6H_4Cl}\end{array} + \mathrm{Pd^0} \qquad (4)$$



$$\mathrm{Pd^0} + 2\mathrm{C_6H_5Cl} \longrightarrow \begin{array}{c}\mathrm{C_6H_5}\\ | \\ \mathrm{C_6H_5}\end{array} + \mathrm{Pd^{+2}} + 2\mathrm{Cl^-} \qquad (5)$$

Pd-Catalyzed Reductive Coupling of Halobenzenes. Recently, we demonstrated that heterogeneous Pd/C is an efficient catalyst for the reductive homocoupling of halobenzenes in both aqueous and organic media, in which catalyst regeneration can be effected using various reductants, e.g., formate ions,[10a] H_2 gas,[10b] or zinc powder.[11] Here, too, it is advantageous to examine the analogous reaction using stoichiometric amounts of Pd/C, namely $2C_6H_5X + Pd^0 \rightarrow C_6H_5{-}C_6H_5 + Pd^{2+} + 2X^-$ (wherein X = Cl, Br, I) in which a quantitative yield of biphenyl is obtained. We believe that this reaction proceeds via two consecutive single-electron-transfer (SET) processes from a palladium site to two substrate molecules, generating two $[C_6H_5X]^{-\bullet}$ radical anions. Subsequent ejection of X^- anions[15] and coupling of the phenyl radicals affords PdX_2 and biphenyl.[16] Fortunately, this system enables coupling of chlorobenzenes (as opposed to most other catalytic reductive coupling procedures, which require the use of bromo- or preferably iodobenzenes), because the bulky $PdBr_2$ and PdI_2 will not react with benzene to form biphenyl.[12]

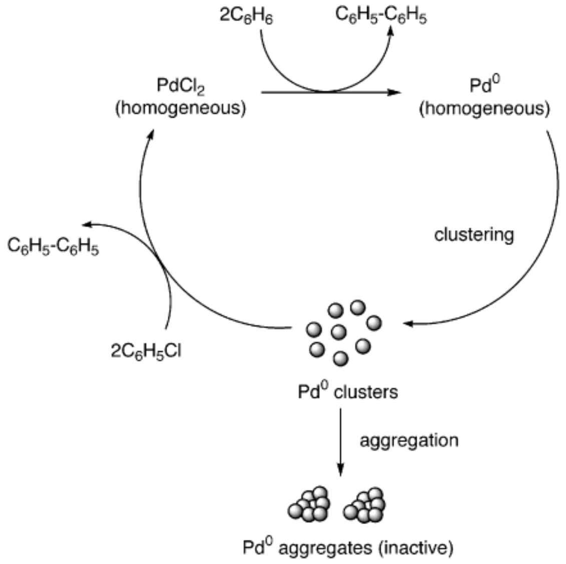


Figure 1. Cycle combining oxidative coupling of benzene, reductive coupling of chlorobenzene, and catalyst deactivation through aggregation.

The successful combination of the oxidative and reductive coupling reactions depends therefore on the formation of an active heterogeneous catalytic species. The problem is that when the Pd^0 becomes truly heterogeneous, i.e., precipitates as Pd metal on the bottom of the reactor, it is no longer active. However, precipitation of Pd^0 out of the reaction mixture is unlikely to be an instantaneous process, as the Pd^0 atoms are thought to be formed individually (one Pd^0 atom per oxidative coupling reaction). A similar phenomenon was observed by Mandai et al. with regard to the reduction of $Pd(OAc)_2$ with $n\text{-}Bu_3P$, wherein after 30 min all of the active Pd^0 catalyst was deactivated as solid black palladium particles.[17] It is therefore possible to envisage catalyst deactivation as a two-stage process: clustering of Pd^0 atoms to form small, soluble clusters, followed by aggregation of these clusters to form large insoluble Pd^0 aggregates which precipitate out of the reaction mixture. Some indication as to the rate of formation of the inactive palladium aggregates was obtained from a blank reaction, to which C_6H_5Cl was added only after 10 min stirring of the other reaction components. No reaction was observed in this case, indicating the fast deactivation of the catalyst in the absence of chlorobenzene.

We suggest that the Pd^0 clusters, being soluble and having a high surface area, could catalyze the reductive coupling of C_6H_5Cl, with concurrent regeneration of the homogeneous $PdCl_2$ (see Figure 1). Evidence supporting this hypothesis was obtained from experiments using different kinds of Pd^0 catalysts (Table 1, entries 20 and 21). While no reaction was observed in the presence of Pd/C, equivalent catalytic amounts of a colloid dispersion of Pd^0 particles *did* catalyze the reaction. (The lower conversion observed using colloid palladium as catalyst might be due to facile aggregation of Pd^0 colloid particles compared to that of homogeneous "just formed" Pd^0 atoms.) Furthermore, it can be argued that catalytic

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(14) Dehm, H. C.; Chien, J. C. *J. Am. Chem. Soc.* **1960**, *82*, 4429.

(15) For recent studies on this specific bond scission, see (a) Pierini, A. B.; Duca, J. S., Jr.; Vera, D. M. A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1003. *(b)* Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 7158.

(16) A similar mechanism was suggested for the Pd-catalyzed coupling of halopyridines: Munavalli, S.; Rossman, D. I.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K.; Ferguson, C. P.; Grätzel, M. *J. Fluor. Chem.* **1995**, *73*, 1.

(17) Mandai, T.; Matsumoto, T.; Tsuji, J.; Saito, S. *Tetrahedron Lett.* **1993**, *34*, 2513.

amounts of THAC (Table 1, entries 10−14) facilitate conversion without affecting product selectivity because THAC stabilizes the small palladium clusters and retards catalyst deactivation caused by aggregation. Indeed, stabilization of Rh^0 and Pd^0 clusters using quaternary ammonium salts has been discussed at length,[18a−c] and their roles in regenerating $PdCl_2$ from Pd^0 complexes using 1,2-dichloroethane has also been studied.[18d,e] The solvent apparently plays a similar role (Table 1, entries 16−18).

The typical pseudo first-order rate constants observed in this tandem system ($k_{obs} \sim 10^{-6}\ s^{-1}$) are significantly lower than those observed in any of the reductive or oxidative parent systems. Thus, for the stoichiometric reaction $2C_6H_6 + PdCl_2 + 2NaOAc \rightarrow C_6H_5{-}C_6H_5 + Pd^0 + 2NaCl + 2AcOH$, $k_{obs} \sim 10^{-3}\ s^{-1}$ (ref 12); for the stoichiometric reaction $2C_6H_5Cl + Pd^0 \rightarrow C_6H_5{-}C_6H_5 + Pd^{2+} + 2Cl^-$, $k_{obs} \sim 10^{-3}$ - $10^{-4}\ s^{-1}$ (ref 10a); and for the palladium-catalyzed reductive coupling of chlorobenzenes $k_{obs} \sim 10^{-3}$ - $10^{-4}\ s^{-1}$ (depending on the reagent used to regenerate the Pd^0 catalyst).[10b,11] This may reflect the low concentration of the active palladium clusters required to catalyze the reductive coupling.

Another route to biphenyl may be envisaged through formation of PhPdCl, followed by cross coupling as in PhPdCl + PhH → Ph-Ph + Pd(0) + HCl. However, though bromobenzene and iodobenzene undergo Heck-type reactions with a catalytic amount of Pd and with styrene, chlorobenzene cannot. Indeed, such a reaction would be potentially useful for mild cross-coupling of chloroaryls as in PhPdCl + PhMe → Ph−PhMe + Pd(0) + HCl, but unfortunately, when we tried it, it did not work.

Conclusion

Two noncatalytic processes, the homogeneous oxidative homocoupling of benzene to biphenyl using $PdCl_2$, and the reductive heterogeneous homocoupling of chlorobenzene (also to biphenyl) using Pd^0, can be combined in situ to obtain a closed catalytic cycle based on the $Pd^{2+} \Leftrightarrow Pd^0$ redox transformation. A key feature of this system is the interchanging of the palladium catalyst between homogeneous ($PdCl_2$) and heterogeneous (Pd^0) forms. The concept of two different substrates “converging” on the same is a step toward waste minimization. In this study, the cheaper, but normally inactive, aryl *chlorides* were employed. Practical application of this process is limited (to a certain extent by its own mechanism), by low catalyst turnover and moderate yields, compared with either the reductive or the oxidative stoichiometric processes. Optimizing applications of this concept to other substrates requires further research, which is currently in progress in our lab.

Experimental Section

Instrumentation, experimental apparatus, and product isolation and identification methods have been described in detail previously.[10,11]

Preparation of a Colloidal Dispersion of Pd^0 in Benzene. This is a modification of a published procedure.[19] An aqueous solution of 0.53 g of (14 mmol) $NaBH_4$ was added dropwise over 1 h to a reaction mixture containing 0.50 g (2.8 mmol) of $PdCl_2$, 1.0 g (2.3 mmol) of THAC, and 10 g of C_6H_6 at 27 °C. The mixture was stirred for 2 h, after which the benzene layer after phase separation was directly taken for the reaction.

General Procedure for Coupling. Example: biphenyl from C_6H_6 and C_6H_5Cl. Amounts of 7.8 g (100 mmol) of C_6H_6, 11.27 g (100 mmol) of C_6H_5Cl, 1.0 g (2.3 mol %) of THAC, 0.5 g (2.8 mol %) of $PdCl_2$, 13.6 g (100 mmol) of NaOAc, and 40 mL of AcOH were charged to an autoclave as above. Reaction progress was monitored by GC. The mixture was stirred (1000 rpm) at 105 °C for 36 h and cooled, and the solvent was removed by distillation. Water (30 mL) was added, and the product mixtures were extracted in of $CHCl_3$ (4 × 15 mL). Solvent evaporation and recrystallization afforded 4.6 g of biphenyl (30 mol % based on C_6H_6; repeating the reaction four times gave 27%, 29%, 28%, and 28%, respectively), mp 68.5 °C (from cold EtOH) (lit.,[20] 69−71 °C). Found: C, 93.27; H, 6.68. $C_{12}H_{10}$ requires C, 93.46; H, 6.54%. δ_H ($CDCl_3$; Me_4Si) 7.37 (2H, tt, aromatic 4,4′-H, *J* 7.2 and 1.3), 7.46 (4H, tt, aromatic 3,3′,5,5′-H *J* 7.1 and 1.0), 7.58 (4H, dq, aromatic 2,2′,6,6′-H *J* 7.0 and 1.2). Good agreement was found with literature values.[21]

Experimental Procedure for Kinetic Studies. Conditions and apparatus were similar to general coupling procedure given above. The following parameters were studied: (i) benzene concentration, (three experiments at 2.0 M, $k_{obs} = 4.55 \times 10^{-6}\ s^{-1}$, $r^2 = 0.995$ for 7 observations; 2.5 M, $k_{obs} = 4.97 \times 10^{-6}\ s^{-1}$, $r^2 = 0.999$ for 7 observations; and 3.0 M, $k_{obs} = 5.19 \times 10^{-6}\ s^{-1}$, $r^2 = 0.998$ for seven observations); (ii) chlorobenzene concentration, (three experiments at 2.0 M, $k_{obs} = 4.58 \times 10^{-6}\ s^{-1}$, $r^2 = 0.997$ for 7 observations; 2.5 M, $k_{obs} = 4.94 \times 10^{-6}\ s^{-1}$, $r^2 = 0.999$ for seven observations; and 3.0 M, $k_{obs} = 5.33 \times 10^{-6}\ s^{-1}$, $r^2 = 0.994$ for seven observations); (iii) initial $PdCl_2$ loading, (four experiments using 0.0175 M, $k_{obs} = 1.25 \times 10^{-6}\ s^{-1}$, $r^2 = 0.995$ for seven observations; 0.035 M, $k_{obs} = 2.4 \times 10^{-6}\ s^{-1}$, $r^2 = 0.997$ for seven observations; 0.07 M, $k_{obs} = 4.97 \times 10^{-6}\ s^{-1}$, $r^2 = 0.999$ for seven observations; and 0.14 M, $k_{obs} = 9.7 \times 10^{-6}\ s^{-1}$, $r^2 = 0.999$ for seven observations); and (iv) reaction temperature, (four experiments at 75 °C, $k_{obs} = 1.13 \times 10^{-6}\ s^{-1}$, $r^2 = 0.98$ for seven observations; 85 °C, $k_{obs} = 2.0 \times 10^{-6}\ s^{-1}$, $r^2 = 0.997$ for seven observations; 95 °C, $k_{obs} = 2.97 \times 10^{-6}\ s^{-1}$, $r^2 = 0.997$ for seven observations; and 105 °C, $k_{obs} = 4.97 \times 10^{-6}\ s^{-1}$, $r^2 = 0.999$ for seven observations).

Acknowledgment. We are grateful to Dr. Dave J. Adams (York Green Chemistry Group, The University of York) for valuable comments and to Dr. Jacques Muzart (University of Reims) for discussions and preprints. G.R. thanks the Royal Society and the Israeli Academy of Sciences and Humanities for an exchange fellowship to visit the York Green Chemistry Group.

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