Kinetic study of the oxidative addition of methyl iodide to Vaska's complex in ionic liquids

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Abstract

Oxidative addition of methyl iodide to Vaska's complex in the ionic liquids 1-butyl-3-methylimidazolium triflate [C$_4$mim][OTf], [C$_4$mim] bis(trifluormethylsulfonyl)imide [Tf$_2$N], and N-hexylpyridinium [C$_6$pyr][Tf$_2$N] occurred cleanly to give the expected Ir(III) oxidative addition product. Pseudo-first order rate constants were determined for the oxidative addition reaction in each solvent ([Vaska's] = 0.25 mM, [CH$_3$I] = 37.5 mM). The observed rate constants under these conditions were 5–10 times slower than the rate seen in DMF. At high methyl iodide concentrations (>23 mM), the expected first order dependence on methyl iodide was not observed. In each ionic liquid, there was no change in the reaction rates within experimental error over the methyl iodide concentration range of 23–75 mM. At lower methyl iodide concentration, a decrease in rate was observed in [C$_4$mim][Tf$_2$N] with decreasing concentration of methyl iodide.
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Keywords: Oxidative addition; Vaska's complex; Ionic liquid; Kinetics

1. Introduction

Ionic liquids (ILs) have received a significant amount of recent attention as alternative solvents for metal-catalyzed reactions [1–4]. ILs have a number of properties that make them potentially attractive alternatives to traditional organic solvents, including low volatility, flammability, and in some cases low toxicity, which are attractive properties for large scale application. The miscibility properties of ILs with water and organic solvents can be tuned over a wide range by appropriate choice of cation and anion. Of particular interest for application to homogeneous catalysis are the solvation properties of ILs. A number of workers have tried t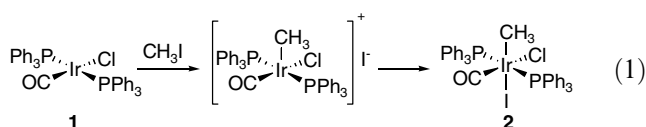o quantify the polarity of imidazolium-based ionic liquids using solvochromatic dyes [5–15], chemical equilibria [16], reaction selectivity [17], partitioning studies [18], and multiple term linear free energy relationships [19,20]. The general consensus of this work is that the polarity of ILs is comparable to short chain alcohols or aprotic dipolar solvents, such as DMF or DMSO. Unlike polar molecular solvents, ILs are weakly coordinating solvents if low nucleophilicity anions are used [8]. This combination of polarity and low coordinating ability is unprecedented among typical molecular solvents.

Although ILs have been promoted as "designer solvents," little is known about how IL solvent properties affect fundamental reactions. Welton and co-workers [21–23] has studied S$_N$2 substitution reactions with halide nucleophiles. Halides were found to be less nucleophilic in imidazolium ILs than in aprotic molecular solvents, presumably due to the ability of the IL cation to hydrogen bond with the halide anion. Although ILs have been used in a variety of metal-catalyzed processes,

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there are few examples of careful mechanistic or kinetic studies of organometallic reactions in ILs [24–28]. A better understanding of how ILs affect the rate and mechanism of fundamental organometallic processes will allow ILs to be more rationally chosen to promote specific catalytic processes.

Herein we report the details of a kinetic study of the oxidative addition of methyl iodide to Vaska's complex (**1**) in ionic liquid solvents (Eq. (1)) [29–32]. We chose this reaction because it is well understood to proceed by an S_N2 mechanism that involves the rate limiting formation of a cationic five-coordinate Ir(III) intermediate. The cationic intermediate could potentially be stabilized by the IL, thus accelerating the oxidative addition reaction. Furthermore, the rate of the oxidative addition reaction has been measured in a range of organic solvents [31], where it shows a strong acceleration in polar solvents. Therefore, we hoped that by comparing rates of the reaction in ILs with known values determined in organic solvents, we could compare the solvent effect of ILs on this reaction to well known organic solvents.

$$
\begin{array}{ccc}
\underset{\substack{OC}}{\overset{\substack{Ph_3P}}{\diagdown}} Ir \underset{\substack{PPh_3}}{\overset{\substack{Cl}}{\diagup}} & \xrightarrow{CH_3I} & \left[\underset{\substack{OC}}{\overset{\substack{Ph_3P}}{\diagdown}} Ir \underset{\substack{PPh_3}}{\overset{\substack{CH_3 \\ Cl}}{}} \right]^+ I^- \longrightarrow \underset{\substack{OC}}{\overset{\substack{Ph_3P}}{\diagdown}} Ir \underset{\substack{PPh_3}}{\overset{\substack{CH_3 \\ Cl \\ I}}{}} \quad (1) \\
\mathbf{1} & & \mathbf{2}
\end{array}
$$

2. Results

The ILs used in this study, 1-butyl-3-methylimidazolium triflate [C$_4$mim][OTf], 1-butyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide [C$_4$mim][Tf$_2$N], and *N*-hexylpyridinium bis(trifluormethylsulfonyl)imide [C$_6$pyr][Tf$_2$N] (Fig. 1), were synthesized using the literature procedures [5,33]. The ILs were dried under vacuum at 70 °C for 24 h and then stored and dispensed in a glove box. When necessary, the ILs were decolorized using activated carbon and/or alumina, which gave colorless to very pale yellow ILs. Water content for the ILs was determined to be 249 ([C$_4$mim][TfO]), 75 ([C$_4$mim][Tf$_2$N]), and 55 ([C$_6$pyr][Tf$_2$N]) ppm by Karl Fischer titration. The ILs were determined to be spectroscopically pure as determined by ^{1}H, ^{13}C, ^{19}F NMR spectroscopy.
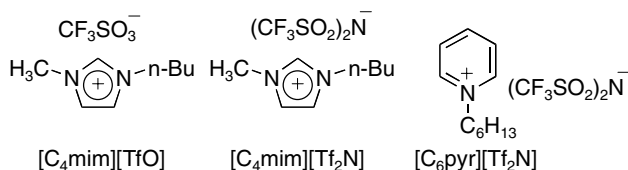
Vaska's complex is slightly soluble in the ionic liquids tested. Heating a suspension of Vaska's complex in the ILs while stirring vigorously lead to homogeneous 0.25 mM solutions after several hours. Once dissolved, the Vaska's complex remained in solution indefinitely even after the solution was allowed to cool to room temperature. The ^{31}P NMR spectrum of a solution of Vaska's complex in [C$_6$pyr][Tf$_2$N] gave a single, sharp resonance at 24.5 ppm, which is nearly identical to the chemical shift measured in DMF. Stock solutions stored for several weeks under nitrogen in a glove box showed no signs of degradation by ^{31}P NMR spectroscopy. Methyl iodide solutions up to 75 mM could easily be formed after mixing for a few seconds. These solutions remained homogeneous even after storing at −30 °C for several weeks. ^{2}H NMR spectroscopic analysis of a solution of CD$_3$I in [C$_6$pyr][Tf$_2$N] gave the expected signal at 1.9 ppm.

To ensure that the oxidative addition reaction would occur cleanly in ILs, a solution of Vaska's complex in [C$_6$pyr][Tf$_2$N] was treated with an excess of methyl iodide under nitrogen in a septum-sealed NMR tube. The reaction was analyzed by ^{31}P NMR spectroscopy after 18 h. The Vaska's complex peak was no longer present and a new resonance appeared at −18.7 ppm as the only phosphorus-containing species present in solution. To confirm the identity of this resonance as the oxidative addition product, an authentic sample of **2** was prepared in toluene. After removal of the volatile materials, the oxidative addition product was dissolved in [C$_6$pyr][Tf$_2$N]. Analysis of the solution by ^{31}P NMR spectroscopy gave a single resonance at −18.7 ppm. Based on these results, the oxidative addition occurs cleanly in [C$_6$pyr][Tf$_2$N] without formation of any phosphorus containing side products.

Kinetic studies were performed at 25 °C under pseudo-first order conditions ([CH$_3$I]:[Ir] = 150) by following loss of the Vaska's complex absorbance at 385 nm. The reactions gave linear pseudo-first order decays over 2–3 half-lives in most cases (Fig. 2). In agreement with the NMR data, UV–Vis data showed clean consumption of Vaska's complex, as judged by loss of the peak at 385 nm. The solvent cut-off of the IL solutions prevented observation of the product, but an increase in intensity is seen below 330 nm as the reaction progresses. An isosbestic point was observed at 331 nm (Fig. 3).

To compare the rate of the oxidative addition reaction in IL and molecular solvents, observed rate constants (k_{obs}) were determined in DMF, [C$_6$pyr][Tf$_2$N], [C$_4$mim][TfO], and [C$_4$mim][Tf$_2$N]. In each case, reactions were run with a Vaska's complex concentration of 0.25 mM and methyl iodide concentration of 37.5 mM, with the exception of DMF. Reactions in DMF were too fast to observe under these conditions, and so were run over a range of lower methyl iodide
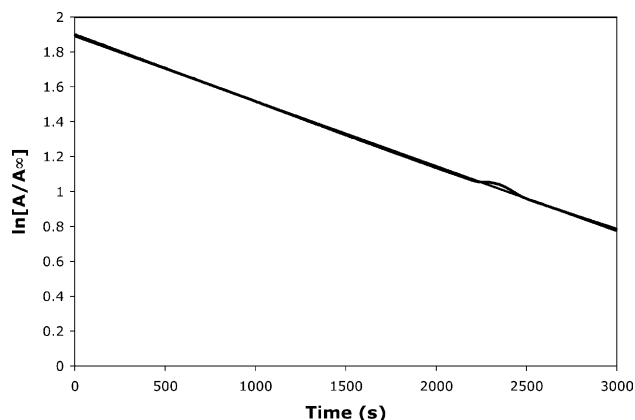
Fig. 1. Ionic liquids used in this study.

Fig. 2. Pseudo-first order plot for reaction of CH_3I and Vaska's complex ([CH_3I]:[Ir] = 150) at 25 °C. Slope = 3.7×10^{-5}, $r^2 = 0.9995$.
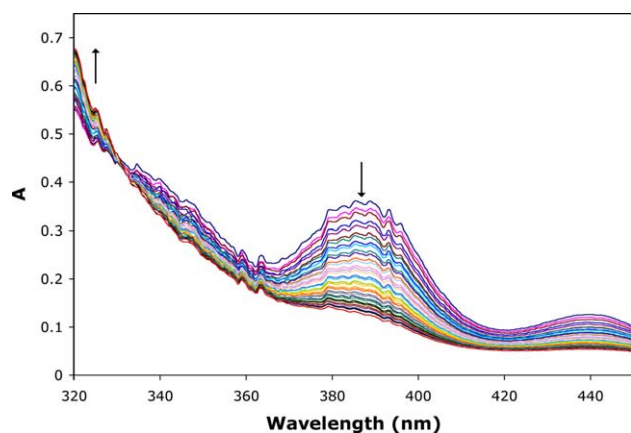

Fig. 3. Stacked plot of UV–Vis spectra for the reaction of CH_3I and Vaska's complex ([CH_3I]:[Ir] = 150) at 25 °C.

Table 1
Pseudo-first order rate constants for oxidative addition of CH_3I to Vaska's complex[a]

Solvent	$k_{obs}(\times 10^4\ s^{-1})$
Toluene	1.3[b]
[C_6pyr][Tf_2N]	1.5 ± 0.4
[C_4mim][TfO]	3.2 ± 0.7
[C_4mim][Tf_2N]	3.6 ± 0.3
DMF	14.9[c]
	10.5[b]

[a] [CH_3I] = 37.5 mM, [Ir] = 0.25 mM, 25 °C.
[b] Literature value [31].
[c] Extrapolated from the measured second order rate constant ($k_2 = 400\ M^{-1}\ s^{-1}$).

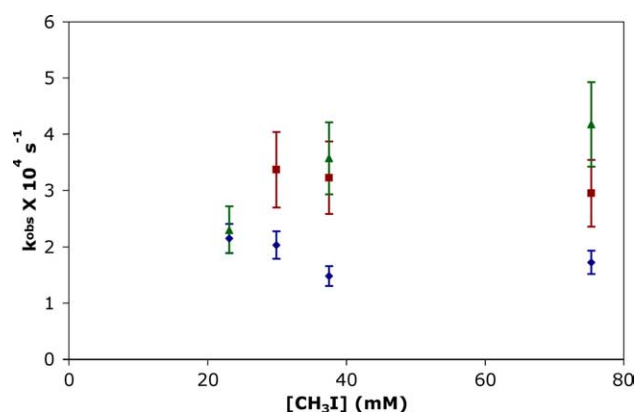Fig. 4. Observe pseudo-first order rate constant ($\times 10^4\ s^{-1}$) vs. [CH_3I]. [Vaska's] = 0.25 mM, 25 °C. [C_6pyr][Tf_2N] (♦), [C_4mim][TfO] (■); [C_4mim][Tf_2N] (▲).

concentrations. An extrapolated k_{obs} was then determined for DMF. The observed rate constant was only slightly larger in [C_6pyr][Tf_2N] than the reported rate constant in toluene [31]. The imidazolium ILs gave rate constants approximately twice the value for [C_6pyr][Tf_2N]. The rate constants for all three ILs were significantly smaller than that for DMF (see Table 1).

In order to obtain second order rate constants, the oxidative addition reaction was run in IL solvents with methyl iodide concentrations ranging from 23 to 75 mM, while the Vaska's complex concentration was maintained at 0.25 mM. A plot of average observed rate constant as a function of methyl iodide concentration is shown in Fig. 4. Surprisingly, the expected first order dependence on methyl iodide concentration was not observed. In the case of [C_6pyr][Tf_2N] and [C_4mim][TfO] there was no change in the observed rate constant within experimental error over this methyl iodide concentration range. In the case of [C_4mim][Tf_2N], an increase in rate was seen upon increasing the methyl iodide concentra-

tion from 23 to 37.5 mM, but a further increase to 75 mM gave only a small, statistically insignificant change in observed rate.

The [C_4mim][Tf_2N] results showed a decrease in rate at the lower end of the concentration range initially tested. Another series of measurements were then made with methyl iodide concentrations ranging from 2.7 to 18.7 mM (Fig. 5). At lower concentration, the observed rate constant does decrease with decreasing methyl iodide concentration. Over the lower concentration range (0–38 mM) the methyl iodide dependence is linear ($r^2 = 0.98$). At higher concentration, a maximum rate is reached that is independent of methyl iodide concentration.

Oxidative addition reactions in [C_4mim][TfO] and [C_6pyr][Tf_2N] appear to reach a maximum rate at lower methyl iodide concentration (23 mM) than was observed with [C_4mim][Tf_2N] (38 mM). A series of oxidative addition reactions in [C_6pyr][Tf_2N] at 12 mM methyl iodide gave an observed rate constant of $0.54 \times 10^{-4}\ s^{-1}$, which was significantly lower than the observed rate constant seen with methyl iodide concentrations $\geqslant 23$ mM. Thus, there appears to be a similar saturation kinetic profile to
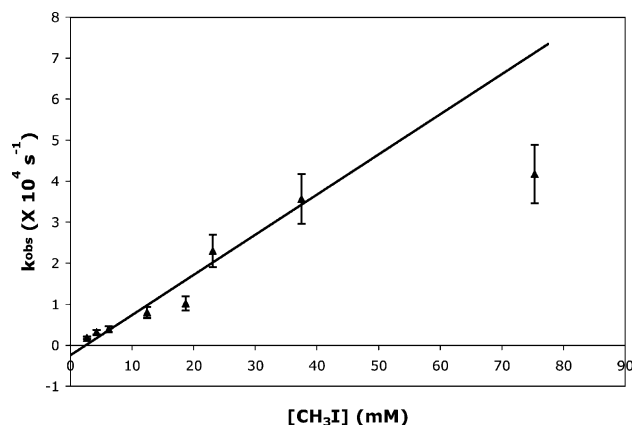
Fig. 5. Observed rate constant ($\times 10^4$ s^{-1}) vs. [CH$_3$I] in [C$_4$mim][Tf$_2$N]. [Vaska's] = 0.25 mM, 25 °C. Line shows linear regression over [CH$_3$I] = 2.7–37.5 mM (slope = 0.10 mM^{-1} s^{-1}, r^2 = 0.98).

that seen with [C$_4$mim][Tf$_2$N], but with the saturation occurring at lower methyl iodide concentration.

We considered several possible explanations for the observed rate profile: (1) mass transport limited rate at high methyl iodide concentration; (2) a decrease in solvent polarity at high methyl iodide concentration; (3) a change in mechanism from a simple second order substitution reaction. Mass transport limited rates can be eliminated as a possibility, since the stock solutions and combined reaction mixtures were always homogeneous. We saw no evidence that methyl iodide was immiscible with the ILs over the concentration range used in these studies. Even after standing at −30 °C, 75 mM methyl iodide solutions remained homogeneous. Similarly, Vaska's complex remained in solution once dissolved in each of the ILs.

In order to determine if solvent properties were changed due to methyl iodide addition, Kamlett–Taft parameters were determined in mixtures of [C$_6$pyr][Tf$_2$N] using Reichert's dye, 4-nitroaniline (4NA), and 4-nitro-N,N-dimethylaniline (4NDMA) [34,35]. The λ_{max} values for the three dyes are sensitive to solvent polarity/polarizability, hydrogen bond donor, and hydrogen bond acceptor properties. Thus, if addition of methyl iodide affected the solvent properties, a change in λ_{max} should be observed. Methylene chloride was used as the nonpolar component in place of methyl iodide to avoid reactions with the aniline probe dyes. Solutions of each of the three dyes were prepared in [C$_4$mim][Tf$_2$N] containing 0, 4, or 38 mM methylene chloride. No change was observed in the λ_{max} for any of the probe dyes as the amount of methylene chloride was increased (Table 2). Therefore, it appears unlikely that the observed rate saturation could be due to changes in the solvent properties over the range of methyl iodide concentrations used.

With other possible explanations eliminated, we concluded that the observed kinetic profile was consistent with a change from the expected simple S$_N$2 mechanism.

Table 2
Solvatochromic dye absorption maxima in CH$_2$Cl$_2$/[C$_4$mim][Tf$_2$N]

|	No CH$_2$Cl$_2$ (nm)	4 mM CH$_2$Cl$_2$ (nm)	38 mM CH$_2$Cl$_2$ (nm)
Reichert's dye	555	553	555
4NA[a]	367	366	367
4NDMA[b]	409	408	409

[a] 4-Nitroaniline.
[b] N,N-Diethyl-4-nitroaniline.

We propose that the oxidative addition is promoted by reversible ligand coordination to Vaska's complex (Scheme 1). Thus, in addition to the usual second order reaction between methyl iodide and Vaska's complex (path A), there would be a second pathway involving coordination of a ligand species to Vaska's complex (path B). This 5-coordinate species would then undergo oxidative addition of methyl iodide. The combined rate expression for pathways A and B are shown in Eq. (2). Significantly, the path B term would be independent of methyl iodide at high concentration (k_3[CH$_3$I] $\gg k_{-2}$).

$$\text{Rate} = k_1[\text{CH}_3\text{I}][\text{Ir}] + \frac{k_2 k_3[\text{CH}_3\text{I}][\text{L}][\text{Ir}]}{k_{-2} + k_3[\text{CH}_3\text{I}]} = k_{\text{obs}}[\text{Ir}] \qquad (2)$$

$$k_{\text{obs}} = k_1[\text{CH}_3\text{I}] + \frac{k_2 k_3[\text{CH}_3\text{I}][\text{L}]}{k_{-2} + k_3[\text{CH}_3\text{I}]} \qquad (3)$$

However, for the observed rate constant (Eq. (3)) to be methyl iodide independent at high concentration, path A must not be kinetically significant (Eq. (4)). For a saturation kinetics expression of this type, a plot of 1/k_{obs} versus 1/[CH$_3$I] should be linear (Eq. (5)). When the data in Fig. 5 (0–38 mM CH$_3$I) was plotted in this manner, a linear dependence was obtained (Fig. 6). The linear relationship of 1/k_{obs} versus 1/[CH$_3$I] is consistent with the rate expression derived from the proposed mechanism
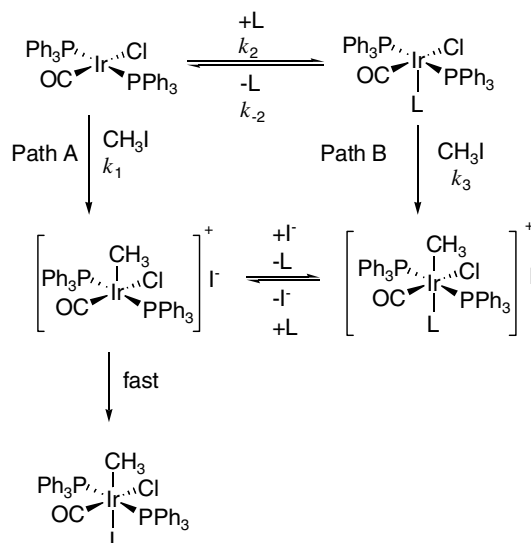
Scheme 1. Proposed mechanism.

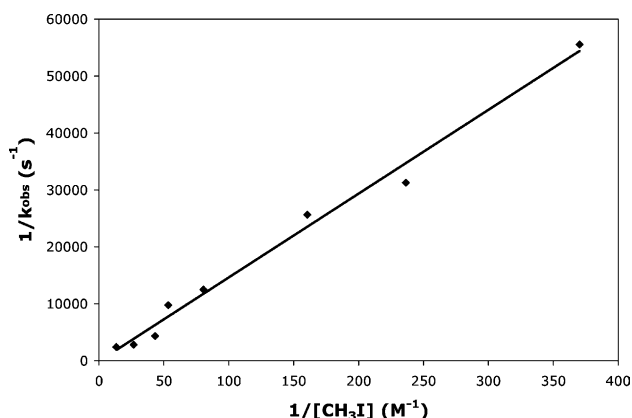Fig. 6. Plot of $1/k_{obs}$ (s) vs. $1/[CH_3I]$. Slope = 148 s M^{-1}, y-intercept = −400 s, r^2 = 0.990.

(Eq. (2)). The y-intercept is negative (−400 ± 1000 s), but with a relatively large standard error. Since the $(k_2[L])^{-1}$ term cannot be negative, it must be relatively small (<10^3), which would require $k_2[L] \geqslant 10^{-3}$ s^{-1}.

$$k_1[CH_3I] \ll \frac{k_2k_3[CH_3I][L]}{k_{-2} + k_3[CH_3I]}$$

$$k_{obs} \approx \frac{k_2k_3[CH_3I][L]}{k_{-2} + k_3[CH_3I]} \qquad (4)$$

$$\frac{1}{k_{obs}} = \left(\frac{k_{-2}}{k_2k_3[L]}\right)\frac{1}{[CH_3I]} + \frac{1}{k_2[L]} \qquad (5)$$

Since halides are known to accelerate the oxidative addition of methyl iodide to Vaska's complex [36], residual halide concentration was determined with an ion-selective electrode. The two batches of $[C_4mim][Tf_2N]$ used in this study gave 1.08 and 2.71 mM halide, respectively. Thus, the halide is present in 4- to 10-fold excess relative to the metal. It is unclear if halide is truly involved, as the observed rates in the higher-halide content sample were not significantly different from those obtained with the lower halide material. Attempts to explore halide effects at higher halide (I^-) concentrations were not possible due to the background absorbance of the halide at 385 nm.

3. Discussion

Oxidative addition of methyl iodide occurs cleanly in IL solvents to give the expected oxidative addition product. Comparison of reaction rates under identical condition, shows that ILs gave only slightly faster rates than toluene. The relatively slow rates measured in IL solvents compared to DMF were surprising, since by most measures ILs have similar polarities to DMF. Rate constants for oxidative addition of methyl iodide to Vaska's complex are known to track linearly with solvent polarity in molecular solvents [31]. A direct

comparison of the observed rate constants is complicated by the fact that reactions in ILs do not appear to follow the same mechanism as that seen in organic solvents, though.

Among the ILs solvents tested, the maximum reaction rate was approximately twice as fast in the imidazolium ILs as in $[C_6pyr][Tf_2N]$. In the imidazolium ILs, changing from triflate to $[Tf_2N]$ had a negligible effect on the observed reaction rate. Typically anion effects are dominant in ILs, but in this reaction the choice of cation appears to have the most significant effect. The major difference between the imidazolium and pyridinium cations is the stronger hydrogen bond donor character of the imidazolium cation. It is possible that imidazolium cation could stabilize the iodide leaving group in the oxidative addition transition state, resulting in faster rates. Further analysis with a wider range of cations and anions will be necessary to more fully understand this difference.

The non-linear dependence of observed rate on methyl iodide concentration is the most interesting observation in this work. Observation of a non-S_N2 oxidative addition mechanism is unusual for Ir(I) or Rh(I) square planar complexes [37]. Examples in which a competing first order process or saturation kinetics are observed, involve participation of solvent as an activating ligand [38,39]. We have proposed a ligand-promoted oxidative addition as an alternative to the direct S_N2 route (Scheme 1). The identity of the activating ligand is unknown, however.

Potentially coordinating species known to be in the IL solutions include the IL anion, halide, and water. The IL anion is present in high concentration (3.5 M in $[C_4mim][Tf_2N]$). The fact that $[C_4mim][TfO]$ and $[C_4mim][Tf_2N]$ gave nearly identical oxidative addition rates would suggest that solvent anion coordination does not play a significant role, however. Triflate would be expected to be more strongly coordinating than bis(trifyl)imide. Halides are known to accelerate oxidative addition of methyl iodide to Ir(I) centers [36]. Halide, presumably bromide, was found to be present in millimolar concentrations in the $[C_4mim][Tf_2N]$ used in this study. The fact that similar rates were measured for two batches of $[C_4mim][Tf_2N]$ with halide concentrations that differed by nearly a factor of three (2.7 versus 1.1 mM) does not seem to support halide being the L in Eq. (2).

Water is also present in appreciable concentration, with a maximum concentration of 18 mM in $[C_4mim][TfO]$. Thus it is possible that water is acting as the activating ligand in these reactions. Methanol coordination has been reported to give saturation kinetics in oxidative addition of methyl iodide to a Rh(I)–pincer complex [39]. There is not a significant effect of the water concentration on the oxidative addition rate, however. $[C_4mim][Tf_2N]$ (5.7 mM H_2O) gave a nearly identical

rate to [C$_4$mim][TfO], despite having an approximately 2-fold lower water concentration. Oxidative addition of methyl iodide to a water-soluble version of Vaska's complex in water has been reported, although kinetic data was not provided [40]. Cationic [L$_2$Ir(CO)(CH$_3$)-(H$_2$O)X]$^+$ was observed along with the expected neutral oxidative addition product. Based on our ^{31}P NMR spectroscopic studies, we see no evidence of a similar cationic oxidative addition product.

4. Conclusion

A kinetic study of the oxidative addition of methyl iodide to Vaska's complex in IL solvents has shown an unusual methyl iodide dependence, which suggests an alternative mechanism to the simple S$_N$2 oxidative addition seen in molecular solvents. A ligand-accelerated mechanism that results in a saturation kinetics rate law is proposed. The kinetic data is consistent with the proposed rate law, although the identity of the accelerating ligand is not yet known. Although a number of questions remain to be answered about this system, these results represent a case in which changing from molecular to IL solvents results in a significant change in mechanism. Further studies on the mechanism of oxidative addition in ILs will shed further light on the effects of these unique solvents on fundamentally important organometallic reactions.

5. Experimental

Vaska's complex was purchased from Strem Chemical Company and stored in a nitrogen filled glove box. Methyl iodide was purchased in ampoules from Aldrich and used as received. Methyl iodide and methyl iodide stock solutions were stored under nitrogen at −30 °C in a glove box.

5.1. Ionic liquid preparation

All ionic liquids were prepared by standard procedures [5,33]. ILs were decolorized using neutral alumina and/or activated charcoal to give materials with low absorbances (<0.1 AU) at 385 nm. Ionic liquids were dried in vacuo (<0.1 mm) overnight at 70 °C prior to use. Water contents were determined by Karl Fischer titration. Residual halide content was measured using an ion-selective electrode calibrated with aqueous bromide standards.

5.1.1. [C$_6$pyr][Tf$_2$N]
^{1}H NMR (CDCl$_3$, 360 MHz): δ 8.80 (d, J = 5.6, 2H), 8.48 (t, J = 8.02, 7.40 Hz, 1H), 8.06 (t, J = 7.4, 6.78 Hz, 2H), 4.59 (t, J = 8.02, 7.39 Hz, 1H), 2.00 (br, 2H), 1.30

(br, 6H), 0.86 (t, J = 6.79, 7.39 Hz, 3H). ^{13}C NMR (CDCl$_3$, 90.6 MHz): δ 145.6 144.3, 128.6, 119.8 (q, J$_{C–F}$ = 322 Hz), 62.5, 31.4, 30.8, 25.5, 22.1, 13.6. ^{19}F NMR (CDCl$_3$ 470.5 MHz): δ −79.32. Water content: 55 ppm.

5.1.2. [C$_4$mim][Tf$_2$N]
^{1}H NMR (CDCl$_3$, 360 MHz): δ 8.71 (s, 1H), 7.32 (d, J = 7.32, 2H), 4.17 (t, J = 7.40 Hz), 3.93 (s, 3H), 1.85 (m, 2H), 1.36 (m, 2H), 0.95 (t, J = 7.40 Hz, 3H). ^{13}C NMR (CDCl$_3$, 90.6 MHz): δ 135.6, 123.6, 122.3, 119.7 (q, J$_{C–F}$ = 320 Hz), 49.6, 35.9, 31.7, 19.0, 12.8. ^{19}F NMR (CDCl$_3$, 470.5 MHz): δ −79.55. Water content: 75 ppm. Halide content: Batch 1, 1.08 mM; Batch 2, 2.71 mM.

5.1.3. [C$_4$mim][TfO]
^{1}H NMR (CDCl$_3$, 360 MHz): δ 9.15 (s, 1H), 7.43 (d, J = 9.86 Hz, 2H), 4.2 (t, J = 7.4 Hz, 2H), 3.97 (s, 3H), 1.86 (m, 2H), 1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (CDCl$_3$, 90.6 MHz): δ 135.7, 123.1, 122.0, 120.1 (q, J$_{C–F}$ = 315 Hz), 49.0, 35.5, 31.2, 18.6, 12.5. ^{19}F NMR (CDCl$_3$, 470.5 MHz): δ −78.99. Water content: 249 ppm.

5.2. Preparation of Vaska's complex stock solutions

Vaska's complex (5.9 mg, 7.5 μmol) was placed in a 25 mL volumetric flask under nitrogen and the IL solvent added. The mixture was stirred vigorously while heating at 40–50 °C until the complex had completely dissolved. Once prepared, stock solutions were stored in a nitrogen-filled drybox. Stock solutions were stable over several months.

5.3. General method for kinetics studies

In a glove box, 830 μL (0.249 μmol) of a 0.3 mM Vaska's complex stock solution and 30 μL of methyl iodide stock solution with the appropriate concentration were combined in a 1 mL volumetric flask. The flask was then filled to 1 mL with the appropriate solvent and placed in a 1 mL quartz cuvette, which was sealed with a septum screw-cap. The cell was placed in a UV–Vis spectrometer with a temperature-controlled cell holder pre-equilibrated at 25 °C. After equilibrating for 5 min, the absorbance at 385 nm was observed over a period of approximately 2 h.

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