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Modelling catalytic turnover frequencies in ionic liquids: the determination of the bimolecular rate constant for solvent displacement from $[(C_6H_6)Cr(CO)_2Solv]$ in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate†

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The bimolecular rate constant for solvent displacement, k_2, from $[(C_6H_6)Cr(CO)_2Solv]$ by an incoming ligand has been determined in the room temperature ionic liquid, [bmim][PF_6], and is compared to that for the same process in cyclohexane and dichloroethane.

Room temperature ionic liquids (RTILs) are excellent media in which to carry out transition metal based catalysis.[1] However, there is a lack of quantitative information concerning reaction rate constants and mechanisms in such systems as compared to conventional solvents. There are, of course, several steps in any catalytic cycle that may be influenced by the choice of solvent, any one of which may be rate determining. The obvious starting point for any detailed study investigating RTIL effects on catalytic cycles is to establish the relative ability of a reactant to displace the coordinated RTIL from a transition metal site compared to conventional solvent systems. As specifically noted in a recent review,[1e] no such rate constants have been determined to date. We report here the first value for a bimolecular rate constant for displacement of an RTIL from a transition metal complex and compare our result to those in conventional solvent systems.

We chose $[(C_6H_6)Cr(CO)_2Solv]$ as our model system because it can be readily generated by UV photolysis of $[(C_6H_6)Cr(CO)_3]$.[2] The photo-induced decarbonylation of $[(C_6H_6)Cr(CO)_3]$ in alkane solution yielding a solvent bound intermediate, $[(C_6H_6)Cr(CO)_2\text{-}Solv]$, is well established:[2]

$$[(C_6H_6)Cr(CO)_3] + Solv \longrightarrow [(C_6H_6)Cr(CO)_2Solv] + CO \quad (1)$$

Solvents that are bound weakly in $[(C_6H_6)Cr(CO)_2Solv]$ can be displaced *via* a bimolecular exchange mechanism[2] with a rate constant, k_2:

$$[(C_6H_6)Cr(CO)_2Solv] + L \longrightarrow [(C_6H_6)Cr(CO)_2L] + Solv \quad (2)$$

We therefore carried out a series of laser flash photolysis experiments (LFP)[3] using 355 nm excitation on $[(C_6H_6)Cr(CO)_3]$ in cyclohexane, dichloroethane, methanol and the RTILs [bmim][PF_6] and [bmim][$(CF_3SO_2)_2N$] at 25 °C.[4] Time resolved spectra were determined from point to point under N_2 saturated conditions and k_2 obtained from plots of the observed first order rate constant for the decay of $[(C_6H_6)Cr(CO)_2Solv]$ transients, k_{obs}, as a function of [L], where L = acetonitrile. The results are summarized in Figs. 1 and 2.

The spectrum in cyclohexane is shown in Fig. 1. The transient spectrum recorded 500 ns after the laser pulse is consistent with that previously reported for $[(C_6H_6)Cr(CO)_2(C_6H_{12})]$, with a strong depletion at 340 nm and an isosbestic point at 380 nm.[2] In the presence of acetonitrile reaction (2) occurs, resulting in formation of $[(C_6H_6)Cr(CO)_2(CH_3CN)]$, the spectrum of which can be seen 5 μs after the laser pulse in Fig. 1. This assignment was confirmed by the immediate formation of a spectrum identical to that recorded at 5 μs when $[(C_6H_6)Cr(CO)_3]$ was irradiated in neat acetonitrile. Variation of the concentration of acetonitrile gave $k_2 = 5.0 \times 10^7$ $mol^{-1}\ dm^3\ s^{-1}$ for the displacement reaction at 25 °C. This value may be compared to $k_2 = 1 \times 10^7$ $mol^{-1}\ dm^3\ s^{-1}$ for displacement of cyclohexane by CO obtained by other workers.[2]

The transient spectra in $C_2H_4Cl_2$ and CH_3OH show weak depletions at 340 and 320 nm and isosbestic points at 370 and 350 nm respectively. Neither solvent was displaced by acetonitrile at concentrations up to 5.0 mol dm^{-3} on our time-scales ($<$ 200 μs), suggesting that $k_2 \leq 10^4$ $mol^{-1}\ dm^3\ s^{-1}$ in these cases.

The time dependent spectral behaviour in [bmim][PF_6] was more complex than in conventional organic solvents (Fig. 2). The spectrum recorded after 20 ns shows depletion in the region around 340 nm and an isosbestic point at 370–380 nm. The species responsible for this spectrum decayed *via* first order kinetics

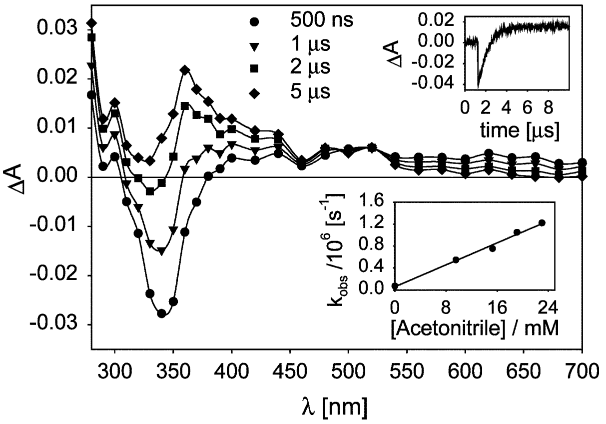

Fig. 1 Transient difference spectrum in cyclohexane, [acetonitrile] = 0.023 mol dm^{-3}. Inset (a); Transient at 350 nm. Inset (b); Plot of k_{obs} *versus* [acetonitrile] at 25 °C, $k_2 = 5.0 \times 10^7$ $mol^{-1}\ dm^3\ s^{-1}$.

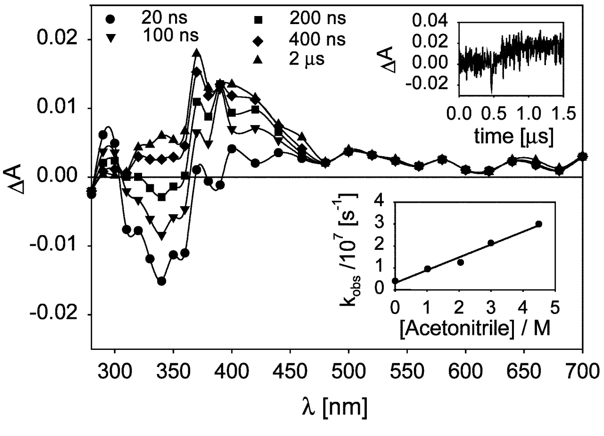

Fig. 2 Transient difference spectrum in [bmim][PF_6]. Inset (a); Transient at 370 nm. Inset (b); Plot of k_{obs} *versus* [acetonitrile] at 25 °C, $k_2 = 5.8 \times 10^6$ $mol^{-1}\ dm^3\ s^{-1}$.

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† Electronic supplementary information (ESI) available: synthesis of RTILs. See http://www.rsc.org/suppdata/cc/b3/b315781d/

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forming a second species with an isosbestic point at 310 nm. The first order rate constant for this process, k_{obs}, measured at 370 nm, was 5×10^6 s^{-1}. We repeated the experiment with water-saturated [bmim][PF_6] (*ca.* 1.5% w/w H_2O),[5] which corresponds to [H_2O] = 1.6 M. An identical product spectrum was observed to grow in more rapidly ($k_{obs} = 8 \times 10^6$ s^{-1}), which strongly suggests that the final product is [$(C_6H_6)Cr(CO)_2(H_2O)$]. From these data we can estimate a bimolecular rate constant $k_2 \approx 5 \times 10^6$ mol^{-1} dm^3 s^{-1} for the reaction of [$(C_6H_6)Cr(CO)_2$(RTIL)] with water. These results clearly show that, despite care being taken to dry the [bmim][PF_6] prior to use and minimal subsequent exposure of the samples to the air, a relatively large amount of water was nevertheless absorbed. Finally, we investigated the reaction of [$(C_6H_6)Cr(CO)_2$(RTIL)] with varying concentrations of acetonitrile in [bmim][PF_6]. A value of $k_2 = 5.8 \times 10^6$ mol^{-1} dm^3 s^{-1}was determined for displacement of [bmim][PF_6], as shown in inset (b) of Fig. 2. It should be noted that this value is around fifty times smaller than that for a diffusion controlled reaction in this solvent.[6]

In principle, both [bmim]$^+$ and [PF_6]$^-$ ions may be initially bound to the [$(C_6H_6)Cr(CO)_2$] intermediate generated immediately after the laser pulse. However, a blue-shifted difference spectrum was obtained on changing the RTIL anion to [$(CF_3SO_2)_2N$]$^-$ with an isosbestic point and depeletion at 350 and 320 nm respectively. Furthermore, we could not displace [bmim][$(CF_3SO_2)_2N$] from [$(C_6H_6)Cr(CO)_2$Solv] at an acetonitrile concentration of 5 mol dm^{-3} which indicates that a more strongly bound [$(C_6H_6)Cr(CO)_2$-Solv] species was now present. Taken together, these observations suggest that binding of the [PF_6]$^-$ anion is responsible for the spectral signature at 20 ns in Fig. 2.

The isosbestic points between [$(C_6H_6)Cr(CO)_2$Solv] and [$(C_6H_6)Cr(CO)_3$] do not show great variation with solvent. However, we can arrive at the approximate spectrochemical series: C_6H_{12} ~ [bmim][PF_6] < $C_2H_4Cl_2$ < CH_3OH < H_2O based on isosbestic points of 380, 370–380, 370, 350 and 300 nm respectively. In an earlier study using a Cu complex which acts as a measure of solvent basicity, it was found that the strength of [PF_6]$^-$ co-ordination to Cu was comparable to or slightly weaker than dichloromethane.[7] Although not overwhelming, the spectroscopic evidence therefore supports the following order of Cr–Solv interaction strength: C_6H_{12} < [bmim][PF_6] < $C_2H_4Cl_2$.

The evidence from solvent displacement kinetics is far less ambiguous; we find that k_2 values for solvent displacement from [$(C_6H_6)Cr(CO)_2$Solv] by acetonitrile follow the trend: C_6H_{12} > [bmim][PF_6] > $C_2H_4Cl_2$. Our results show that the rate constant for displacement of [PF_6]$^-$ from [$(C_6H_6)Cr(CO)_2$Solv] by acetonitrile is up to *two orders of magnitude* greater than that of the next strongest binding solvent in our series, $C_2H_4Cl_2$. Furthermore, it should be reiterated that despite the ‘hydrophobic’ nature of [bmim][PF_6], significant concentrations of H_2O can be present even after careful drying. The result of this is that high concentrations of displacing ligand are required in order to ensure effective competition with displacement by H_2O. Thus, water content might represent a problem in the application of RTILs as solvents in some catalytic systems.

This is a model catalytic system designed purely to ascertain the *relative* ability of a ligand to displace an RTIL from [(C_6H_6)-$Cr(CO)_2$Solv] compared to weakly coordinated conventional solvents. Obviously these results are most pertinent to situations where solvent displacement by a reactant is the rate determining step in the catalytic cycle. It is therefore extremely satisfying to note that enhanced turn over frequencies (TOFs) have been observed for the cationic Ni catalysed oligomerisation of ethene to higher olefins in [bmim][PF_6] compared to that in dichloromethane and butane-1,4-diol (TOF = 12712, 1852 and < 10 h^{-1} respectively).[7] The enhanced TOF in the RTIL was considered to result from a combination of weak binding of [PF_6]$^-$ to the catalytic site and decreased product solubility in this solvent. Our present studies clearly support the former conclusion and also highlight the importance of controlling the water content of RTILs noted by the authors.[8]

In conclusion, we have unambiguously demonstrated that [bmim][PF_6] may be displaced more easily from a ‘vacant’ transition metal binding site of an organometallic complex than even a ‘low polarity’ solvent such as $C_2H_4Cl_2$ and furthermore, that the ease of displacement can be tuned by variation of the RTIL anion. These initial results do not correlate with ligand basicity as measured by β values of these solvents in a simple manner.[9] We are continuing our studies into the mechanism of solvent displacement and dependence of k_2 on the Lewis basicity of the anion, and will present a more detailed report in the near future.

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