Chemical reactivity in ionic liquids: Nitroso group transfer from *N*-nitrososulfonamide

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Nitroso group transfer in ionic liquids exhibits good correlation with the polarity parameters of the ionic liquid, showing that the amine nucleophilicity in not increased on going from water to the ionic liquid.

Ionic liquids (ILs) are attracting increasing attention from chemists and technologists on account of their usefulness as solvents for various processes including catalytic reactions.[1] The interest has partly arisen in the search for "green" industrial solvents. ILs have been advocated as "green solvents" on the grounds of their negligible vapour pressure.[2,3] Many chemists, however, have also realized that ILs possess some unique properties as solvents. Their ease of preparation and structural modification with a view to modulating their physical properties have turned them into a flexible alternative to molecular organic solvents. Although they have proved excellent media for catalytic processes including Friedel–Crafts,[4] alcohol and phenol oxidation,[5,6] Michael addition,[7] fluorination,[8] and enzymatic reactions,[9] in addition to Heck arylation of electron-rich olefins by aryl halides[10] and electrophilic nitration of aromatics,[11] few studies on chemical reactivity in these media have been reported.

Rather, recent research on ILs has focussed on their effects on chemical processes and the potential relationship of such effects to other measurable solvent properties. Thus, Welton and coworkers determined chloride, bromide and iodide nucleophilicity in the reaction of methyl-*p*-nitrobenzenesulfonate in various ILs.[12,13] They found ILs to reduce rather than enhance halide nucleophilicity relative to molecular solvents. The effect of ILs on nucleophilicity can be ascribed to chloride ion being stabilized through hydrogen bonding to the cation in the IL. Halide ions are known to form strong hydrogen bonds[14] with $[\text{bmim}]^+$ and, to a lesser extent, $[\text{bm}_2\text{im}]^+$; on the other hand, [bmpy] cannot be expected to act as a hydrogen bond donor. Changing the anion in an IL has been found to alter the Kamlet–Taft bond acceptor parameter, β.[15] With chloride as the nucleophile, anion and cation effects are similar in magnitude; with bromide and iodide, however, changing the anion in an IL has a more marked effect than replacing the cation. Chiappe and Pieraccini[16] obtained similar results for the reactions of Br_3^- and ICl_2^- with various alkenes and alkynes in ILs. They found the rates of both reactions to increase from 1,2-dichloroethane to the ILs. Available evidence suggests that, while the hydrogen bonding ability of the imidazolium cation is probably the main factor increasing the rate of addition of ICl_2^- to double and triple bonds, this property has no effect on the electrophilic addition of Br_3^- to alkenes and alkynes. Fulfillment of the Hughes–Ingold rules was checked in a study of amine nucleophilicity in both ILs and molecular solvents.[17] All amines studied were found to be more nucleophilic in the ILs than they were in dichloromethane, acetonitrile and water.

In this work, we studied the nitroso group transfer from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) to secondary amines (Scheme 1) in several ILs in order to examine the use of the Kamlet–Taft solvent parameters with a view to estimating chemical reactivity in various media. The amines used [*viz.* morpholine (MOR), *N*-methylpiperazine (MePIP) and pyrrolidine (PYR)], were subject to similar steric hindrance and spanned a wide basicity range (*viz.* pK_a values from 8.36 for MOR to 11.27 for PYR in water).

Kinetic experiments were conducted as described elsewhere,[18] using $\lambda = 390$ nm, $T = 25.0$ °C and MNTS in understoichiometric amounts relative to the amine. All solutions were prepared in the corresponding IL. The moisture content of the amines was minimized by desiccation with CaH_2 and subsequent collection onto a molecular sieve. The IL was prepared in our laboratory, following previously reported procedures[19] and also obtained from Solvent Innovation; the rate constants obtained in the commercially available liquid were always consistent with those determined in the liquid prepared in our laboratory. Absorbance–time data pairs fitted the first-order integral equation well and the pseudo first-order constant values obtained were reproducible to within $\pm 3\%$.

As can be seen from Fig. 1, k_{obs} was always linearly related to the amine concentration. The slopes of the lines were used to obtain the bimolecular rate constants, k. The observed linear relationship between k_{obs} and the amine concentration is consistent with the results obtained in most molecular solvents.[20]

The reactivity sequence in $[\text{bmim}][\text{PF}_6]$ is identical to that in water (*viz.* PYR > MePIP > MOR) and coincides with the sequence of basic strength in the amines. Fig. 2 illustrates the Brønsted plot for this reaction in $[\text{bmim}][\text{PF}_6]$, water[21] and cyclohexane.[20]

The Brønsted slope, α_{nucl}, was 0.79 ± 0.09 in water, 0.76 ± 0.01 in $[\text{bmim}][\text{PF}_6]$ and 0.69 ± 0.03 in cyclohexane. These values were independent of the reaction medium and consistent with a transition state where the nucleophilic attack occurs slightly before the N–N=O bond in the *N*-nitrososulfonamide was cleaved. Table 1 shows the bimolecular rate constants obtained in the studied ILs as well as in other molecular solvents.

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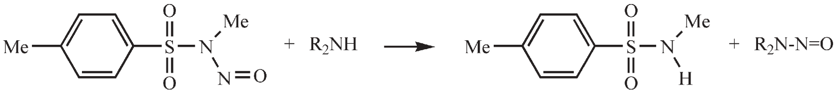

MNTS

Scheme 1

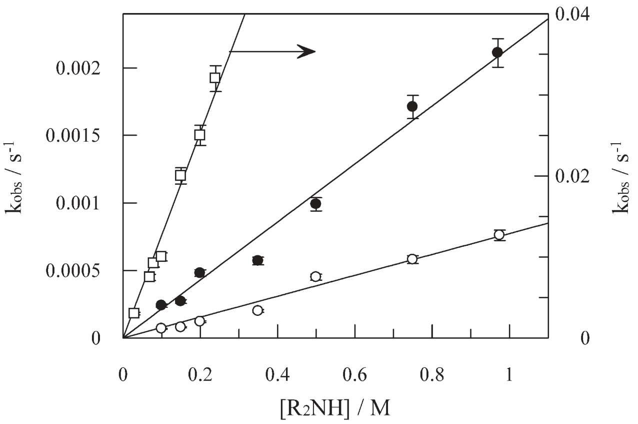

Fig. 1 Influence of the amine concentration on k_{obs} for the the nitroso group transfer from MNTS to secondary amines in [bmim][PF_6] at 25.0 °C. (○) MOR, (●) MePIP, (□) PYR.

Table 1 Bimolecular rate constants for nitroso group transfer from MNTS to pyrrolidine in different solvents. Solvent polarity parameters: polarity/polarizability (π^*); hydrogen bond donating acidity (α) and hydrogen bond accepting basicity (β) are taken from ref. 15*b*

Solvent	Log *k*	π^*	α	β
Water	−0.081	1.09	1.17	0.47
[bmim][BF_4]	−0.903	1.047	0.627	0.376
[bmim][PF_6]	−0.896	1.032	0.634	0.207
[bmim][Tf_2N]	−0.939	0.984	0.617	0.243
[bm_2im][BF_4]	−0.889	1.083	0.402	0.363
Acetonitrile	−1.30	0.75	0.19	0.31
Cyclohexane	−3.51	0.00	0.00	0.00

From Table 1 it follows that the rate constant is almost independent of the ILs for those used in this study. Moreover the rate constant for nitroso group transfer in ILs is roughly one order of magnitude smaller than in water and two orders of magnitude greater than in a very low-polarity solvent such as cyclohexane. Consequently, the nucleophilicity of the amines does not increase from water to an IL. Previous studies carried out by our group[22] showed the validity of the Kamlet–Abboud–Taft equation in explaining the solvent effects on the nitroso group transfer:[23]

$$\log(k/k_0) = s\pi^* + a\alpha + b\beta \tag{1}$$

where k_0 is the rate constant in the reference solvent (cyclohexane in our case), π^* the solvent polarity/polarizability, α the hydrogen bond donating acidity of the solvent, and β its hydrogen bond accepting basicity. Fig. 3 illustrates the very good correlation between $\log(k/k_0)$ and the solvent polarity parameters for isooctane, dioxane, chloroform, methylene chloride, acetonitrile, DMSO and water ($r = 0.997$). It therefore seems that the effect of the solvent on this reaction is due to its dipolarity and, to a lesser extent, its ability to form hydrogen bonds *via* its own protons. The interpretation of solvent effect in terms of dipolarity and hydrogen bond acidity of the solvent can explain why the rate constant is almost independent of the IL for those used in this work.

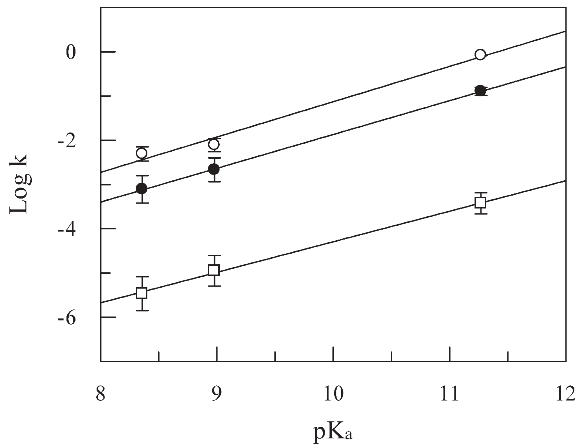

Fig. 2 Brønsted plot for the nitroso group transfer from MNTS to secondary amines in (○) water, (●) [bmim][PF_6] and (□) cyclohexane, all at 25.0 °C.

Fig. 3 shows the $\log(k/k_0)$ for the different ILs in comparison with the correlation obtained for molecular solvents: $\log(k/k_0) = 2.2\pi^* + 0.9\alpha + 0.2\beta$ by using polarity parameters shown in Table 1. As can be seen the rates of nitroso group transfer in the ILs can be predicted very accurately from the reactivity in molecular solvents and the Kamlet–Abboud–Taft equation showing that no specific increase or decrease of amine nucleophilicity can be detected.

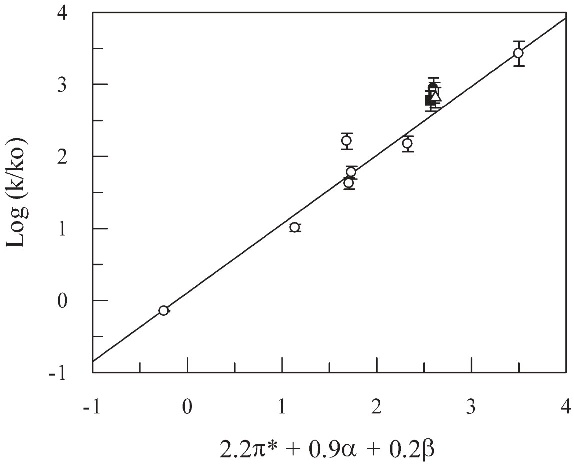

Fig. 3 Plot of $\log(k/k_0)$ against the Taft function for the nitrosation of pyrrolidine by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in various molecular solvents. Values obtained in ILs (●) [bmim][BF_4]; (□) [bmim][PF_6]; (■) [bmim][Tf_2N] and (△) [bm_2im][BF_4] at 25.0 °C.

Previous results obtained by Welton and coworkers[17] for the aminolysis of *p*-nitrobenzenesulfonate by butylamine, dibutylamine and tributylamine in ILs: [bmpy][N(Tf)$_2$], [bmpy][OTf] and [bmim][OTf] have showed that the aminolysis rate constant is one order of magnitude faster in the ILs than in water. Moreover the aminolysis rate constant of methyl-*p*-nitrobenzenesulfonate in water was found to be roughly three times smaller than in acetonitrile. The kinetic behavior observed for the nitroso group transfer is greatly differentiated: the rate constant is 16 times greater in water than in acetonitrile. The different behavior observed for both reactions in molecular solvents should also be responsible for the different kinetic behavior observed in ILs: aminolysis of *p*-nitrobenzenesulfonate is faster in the IL than in water instead of that the nitroso group transfer is slower in the IL than in water. Therefore, available reports on reactivity in ILs must be taken reservedly and any extrapolation to other reactions requires considering the specific behaviour observed in various molecular solvents.

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