

Salts Dissolved in Salts

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Supplemental Information

Details of the computational results

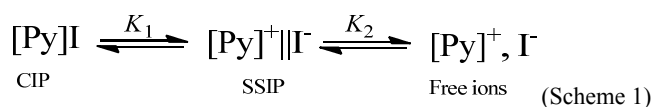
Table S-1 Energy of the metathesis reaction as calculated by DFT and MP2, including the zero point energy and thermal corrections to Gibbs Free Energy (+Z) and basis set superposition error(+B) corrections. The different rows of ΔE and ΔG (kJ/mol) have been calculated from either the most stable ion pairs per complex (MIN), the less stable ion pairs (MAX) or the average Energy of the two (AVR).

	DFT	DFT+Z	DFT+Z+B	MP2	MP2+Z
MIN	-24.10	-24.81	-24.89	-0.84	-0.69
MAX	-23.67	-15.63	-14.68	-18.22	-11.05
AVR	-23.88	-20.22	-19.78	-9.53	-5.87

10

Derivation of equation 1

We can obtain a relationship between the concentration of contact ion pairs (C_{CIP}) and the total concentration of Kosower's complex (C_0) by using a 'double equilibrium' analysis. Using Scheme 1, with ion dissociation constants K_1 and K_2 :



15 Then:

$$K_1 = \frac{C_{SSIP}}{C_{CIP}} \quad (\text{S-1})$$

and:

$$K_2 = \frac{C_{[Py]} * C_I}{C_{SSIP}} \quad (\text{S-2})$$

Assuming all pyridiniums and iodides were added as 1-ethyl-4-(methoxycarbonyl)pyridinium iodide,

$$C_{[Py]} = C_I \quad (\text{S-3})$$

$$C_0 = C_{[Py]} + C_{SSIP} + C_{CIP} \quad (\text{S-4})$$

Rearranging equation (S-1):

$$C_{SSIP} = K_1 * C_{CIP} \quad (\text{S-5})$$

Rearranging equation (S-2):

$$C_{[Py]}^2 = K_2 * C_{SSIP} \quad (\text{S-6})$$

Substituting equation (S-5) into (S-6):

$$C_{[Py]}^2 = K_1 * K_2 * C_{CIP} \quad (\text{S-7})$$

Taking the square root of both sides of equation (S-7):

$$C_{[Py]} = K_1^{0.5} * K_2^{0.5} * C_{CIP}^{0.5} \quad (S-8)$$

Substituting equation (S-8) and (S-5) into (S-4):

$$C_0 = K_1^{0.5} * K_2^{0.5} * C_{CIP}^{0.5} + K_1 * C_{CIP} + C_{CIP} \quad (S-9)$$

Rearranging equation (S-9):

$$(1 + K_1)C_{CIP} + K_1^{0.5} K_2^{0.5} C_{CIP}^{0.5} - C_0 = 0 \quad (1)$$

Derivation of equation 3

Using a simple 3D lattice model, we can determine the probability of a 1-ethyl-4-(methoxycarbonyl)pyridinium cation and an iodide anion being next to each other. We assume that each nearest neighbour pair have opposite charges. Also:

r = number of anions in the solvation shell of a cation

m_T = total number of anions in the system

m_I = total number of iodide ions in the system

The probability that any given anion in the solvation shell of a pyridinium cation is *not* an iodide would be:

$$(m_T - m_I)/m_T \quad (S-10)$$

The probability that *none* of the r anions in the solvation shell of a pyridinium cation are an iodide would be:

$$[(m_T - m_I)/m_T]^r \quad (S-11)$$

Therefore, the probability that at least one of the anions in the solvation shell of a pyridinium cation are an iodide would be:

$$P_{[Py]I} = 1 - [(m_T - m_I)/m_T]^r \quad (3)$$

For $r = 1$ equation (3) can be derived from a simple equilibrium as well. Assuming that the ion pairing of Kosower's Dye in ionic liquids is entirely controlled by statistic, one can write:

$$K = \frac{[PyI] * [C_{0,mim OTf}]}{[Py OTf] * [C_{0,mim I}]} = 1 \quad (S-12)$$

With

C_{PyI} = the concentration of Kosower's Dye ion pairs in contact

$C_{0,PyI}$ = the initial concentration of Kosower's Dye

$C_{0,IL}$ = the initial concentration of ionic liquid

one can write

$$1 = \frac{C_{PyI} * (C_{0,IL} - C_{0,PyI} + C_{PyI})}{(C_{0,PyI} - C_{PyI})^2} \quad (S-13)$$

and therefore

$$C_{PyI} = \frac{C_{0,PyI}^2}{C_{0,IL} + C_{0,PyI}} \quad (S-14)$$

and

$$P_{[Py]I} = \frac{C_{PyI}}{C_{0,PyI}} = \frac{C_{0,PyI}}{C_{0,IL} + C_{0,PyI}} = 1 - \frac{m_T - m_I}{m_T} \quad (S-15)$$

Therefore the statistical lattice model is identical to a chemical equilibrium description for $r=1$.