Is I_2 or MeCN the Better Base to coordinate the Iodine Monocation, I^+? The Hard–Soft Acid—Base Principle in Preparative Inorganic Chemistry

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The quantitative formation of $MeCNI^+$ from MeCN and I_3^+ in SO_2 and the back reaction ($MeCNI^+ + I_2$ gives MeCN + I_3^+) are discussed on the basis of the HSAB principle.

Recently we reported the preparation (isolated yield: 95%) of $MeCNI^+AsF_6^-$ (eqn. 1) which represents the first example of a complex where a nitrogen base is coordinated to the iodine monocation in a 1 : 1 stoichiometry.[1] However, the reaction in eqn. (1) does not follow the predictions of the hard–soft acid–base (HSAB) theory.

$$MeCN + I_3^+AsF_6^- \xrightarrow{SO_2} MeCNI^+AsF_6^- + I_2 \qquad (1)$$

Pearson and Parr expanded the HSAB principle by introducing the absolute electronegativity (χ) and the absolute hardness (η) which have been derived from density functional theory.[2–5] With this concept it is easy to calculate the number of electrons transferred, ΔN (eqn. 2), and the energy change due to charge transfer, ΔE (eqn. 3), caused by interaction of a Lewis acid (A) with a Lewis base (B).

$$\Delta N = (\chi_A - \chi_B)/2(\eta_A + \eta_B) \qquad (2)$$

$$\Delta E = -0.25(\chi_A - \chi_B)^2/(\eta_A + \eta_B) \qquad (3)$$

However, if one calculates the ΔN and ΔE values for the interaction of I^+ with I_2 (eqn. 4) and I^+ with MeCN (eqn. 5), clearly elemental iodine should be a better base to coordinate I^+ than acetonitrile (Table 1) and it is puzzling that $MeCNI^+AsF_6^-$ is formed according to eqn. (1). The driving force for eqn. (1) can be seen in the fact (*i*) that 'pure covalent' N–I bonds [binding energy E_B (N–I) = 156 kJ mol^{-1}, average of E_B(N–N) = 166 and E_B(I–I) 149 kJ mol^{-1}][6] should be slightly

Table 1 Electronegativity and hardness values

	E_I/eV[a]	E_A/eV[b]	χ/eV[c]	η/eV[d]	ΔN[e]	ΔE/kJ mol^{-1}[f]
I_2	9.4	2.6	6.6	3.4		
MeCN	12.2	−2.8	4.7	7.5		
I^+	19.13	10.45	10.79	4.34		
Eqn. (4)					0.55	−240.8
Eqn. (5)					0.42	−207.3

[a] Ionization potential, ref. 3. [b] Electron affinity, ref. 3. [c] Calc. from: $\chi = (E_I + E_A)/2$, ref. 5. [d] Calc. from: $\eta = (E_I - E_A)/2$, ref. 5. [e] Calc. from eqn. (2). [f] Calc. from eqn. (3); 1 J = 0.239 cal.

Table 2 ^{1}H NMR and UV–VIS data

	δ (ppm)[a]			λ_{max}/nm[b]
	SO_2	SO_2ClF	SO_2Cl_2	SO_2Cl_2
I_2				530
I_3^+				470
I_3^+ + MeCN	2.73	2.38[c]	2.39[c]	480
$MeCNI^+$ + I_2	2.73	2.37[c]	2.36[c]	480
MeCN	2.05	2.09	2.12	
$MeCNI^+$	2.73	2.75	2.80	

[a] $SiMe_4$, 25 °C, 60 MHz. [b] $350 \leq \lambda \leq 750$ nm. [c] $MeCN\cdots I_3^+$.

more stable than I–I bonds and (*ii*) that I_2 is more or less insoluble in SO_2 [*cf.* ΔH (I_2, aq. $\rightarrow$ I_2, s) = -23 kJ mol^{-1}].[7] This favours eqn. (1) by 30 kJ mol^{-1} and compensates the missing 33 kJ mol^{-1} due to charge transfer (Table 1).

$$I^+ + I_2 \rightarrow I_3^+ \tag{4}$$

$$I^+ + MeCN \rightarrow MeCNI^+ \tag{5}$$

If these assumptions are correct the reaction according to eqn. (1) should not be possible in a solvent which dissolves all four components. SO_2Cl_2 and SO_2ClF are such solvents. We found out by ^{1}H NMR and UV–VIS spectroscopy (Table 2) (*a*) that MeCN does not react with $I_3^+AsF_6^-$ in SO_2Cl_2 or SO_2ClF (it forms a loose adduct $MeCN\cdots I_3^+$) and (*b*) that $MeCNI^+AsF_6^-$ (prepared in SO_2, eqn. 1) reacts in SO_2Cl_2 with I_2 to yield MeCN and $I_3^+AsF_6^-$ ($MeCN\cdots I_3^+$ adduct). The $MeCN\cdots I_3^+$ adduct is so labile that by pumping off the solvent the MeCN is removed too and pure $I_3^+AsF_6^-$ is isolated ($MeCNI^+AsF_6^-$ is stable in a dynamic vacuum for more than 1 h).[1]

These results are nicely in agreement with both the HSAB principle and simple thermodynamic estimations, and demonstrate that the choice of the solvent can dramatically change the chemistry (SO_2 seems to be optimum if I_3^+ is used as a source of 'I^+'). Eqn. (1) represents an interesting example where an equilibrium can be totally shifted to one or the other side just by changing the solvent. This effect can be predicted on theoretical basis which leads to deeper understanding of reactivity and helps to plan simple inorganic synthesis.

We thank the Deutsche Forschungsgemeinschaft (KL 636-2/1) the Fonds der Chemischen Industrie and the BMBW (Graduiertenkolleg: 'Synthese und Strukturaufklärung niedermolekularer Verbindungen' for financial support. We also thank the BMBW for a graduate scholarship (P. G.).

Received, 3rd July 1990; Com. 0/03001E

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