Is samarium diiodide an inner- or outer-sphere electron donating agent?

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From the measured value of $E°$ (SmI_2^+–SmI_2) in THF and using free energy plots, the electron transfer between samarium diiodide and acetophenone was shown to be clearly of inner-sphere nature; on the other hand, with benzyl bromide it is closer to an outer-sphere process.

Twenty years have almost passed since the first introduction of samarium diiodide (SmI_2) as a reagent for organic synthesis by Kagan and coworkers.[1] The rich chemistry of this polyvalent one-electron reductant has not been surpassed by any other reagent and it still continues to astound with its ability to promote an array of sequential reactions comprising of carbon radicals and anions.[2] It is surprising though that very little is known concerning the mechanistic details of the electron transfer processes (inner- or outer-sphere) taking place between Sm(II) and organic substrates.[3] In this paper, we describe the nature of the electron transfer between SmI_2 and two substrates, namely benzyl bromide and acetophenone.

Paramount for the comprehension of electron transfer processes involving SmI_2, is that the standard potential of the SmI_2^+–SmI_2 couple in THF be well defined. It is noteworthy that these fundamental measurements have not been performed even after 20 years of existence of SmI_2 in the organic chemistry community. The potential cited today by organic chemists for the Sm(III)–Sm(II) couple of −1.80 V *vs.* SCE was determined in 1948 by polarographic measurements in water,[4] which is simply not compatible with current studies.†

Hence, we set out to investigate the redox properties of SmI_2 and SmI_3 by means of cyclic voltammetry in a supporting electrolyte solution of NBu_4I (0.02 M) and NBu_4PF_6 (0.2 M) in THF.‡ Fig. 1 shows three of the voltammograms recorded for SmI_2 at different sweep rates v in the range 0.02–0.5 V s^{-1}. The peak separation increases from *ca.* 150 to 300 mV as a function of v. As the peak potentials and currents acquired in the voltammograms of SmI_2 are in good agreement with the corresponding values obtained for SmI_3, it appears that the same reaction mechanism is in play no matter which of the two compounds is the starting point for the electrochemical investigation. A working model was therefore set up, as illustrated in Scheme 1, involving a heterogeneous electron transfer step and a fast established chemical equilibrium, where SmI_2^+ coordinates strongly with I^- present in the electrolyte solution.

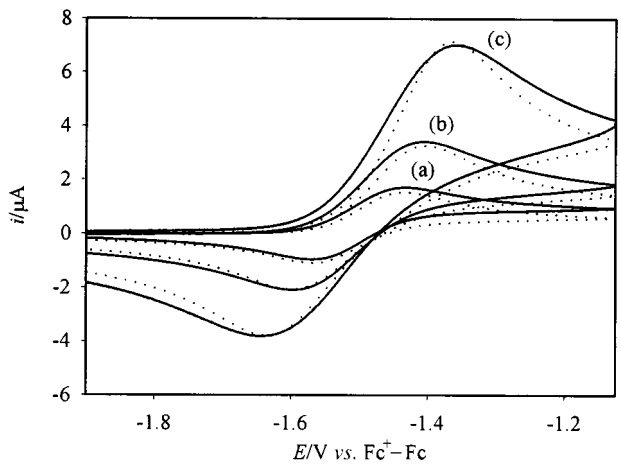

Fig. 1 Cyclic voltammograms of 2.5 mM SmI_2 recorded in THF–0.2 M NBu_4PF_6 + 0.02 M NBu_4I at a glassy carbon electrode (diameter = 1 mm) at sweep rates of (a) 0.02, (b) 0.1 and (c) 0.5 V s^{-1}. The dotted curves represent simulated curves based on the following parameters: $E° = -1.41$ V, $k_f[I^-] = 1.5 \times 10^5$ s^{-1}, $k_b = 3.8 \times 10^3$ s^{-1}, $k° = 0.0065$ cm s^{-1}, $D = 5.4 \times 10^{-6}$ cm^2 s^{-1}, transfer coefficient $\alpha = 0.5$ and capacitance $C_d = 10^{-7}$ F.

$$SmI_2 \rightleftharpoons SmI_2^+ + e$$

$$SmI_2^+ + I^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} SmI_3$$

Scheme 1

In order to determine the standard potential (or more correctly the formal potential) $E°$ of SmI_2^+–SmI_2 from the cyclic voltammograms, the association constant ($K = k_f/k_b$) for SmI_3 is required. A rough estimate of $K \approx 10^7$ dm^3 mol^{-1} could be obtained simply by comparing conductivity measurements performed on SmI_3 and NBu_4I in THF since the association constant for NBu_4I in THF has been estimated previously.[7] However, the electrochemical measurements were carried out with substantial amounts of supporting electrolyte present in THF and K may be somewhat different in this more polar medium. Being cautious and selecting 1 and 10^4 as the limiting values of $K[I^-]$, digital simulations of the voltammograms (see Fig. 1) were carried out on the basis of the above reaction scheme.§ Simulations revealed that $K[I^-]$ is $< 10^4$ if the chemical equilibrium should be established quickly with a large k_b and without k_f exceeding the diffusion-controlled limit. The shape of the experimental cyclic voltammograms was presumably somewhat influenced by adsorption phenomena and therefore the main emphasis in the simulation procedure was to describe the reproducible development in the experimentally obtained peak potentials and currents as a function of v. This led to a value for $E°$ of -1.41 ± 0.08 V *vs.* Fc^+–Fc and for the logarithm of the standard heterogeneous rate constant $k°$ (in cm s^{-1}) of -2.20 ± 0.70. Comparing these values of $E°$ and log $k°$ with those obtained if the chemical equilibrium reaction is neglected (−1.51 V and −2.92, respectively) illustrates the importance of including follow-up or preceding reactions in electrochemical measurements.

The outer- or inner-sphere electron donor abilities of SmI_2 towards a given substrate can now be assessed by comparing the reactivity of SmI_2 and a corresponding outer-sphere electron donor.[8] In this way the degree of electronic interaction between SmI_2 and the substrate in the transition state can be estimated. The first reaction studied was the reduction of benzyl bromide, in which the rate-controlling step is the initial electron transfer forming the benzyl radical. As representatives of outer-sphere electron donors, four radical anions of aromatic compounds were selected having potentials $E°_A$ close to that of SmI_2^+.[8] The rate constants k_{ET} for the electron transfer reactions between the radical anions and benzyl bromide were measured¶ and depicted in free energy plots of log k_{ET} *vs.* $E°_A$ (Fig. 2). The value of k_{ET} (= 0.34 dm^3 mol^{-1} s^{-1}) corresponding to the $E°$ of SmI_2^+ = −1.41 V can be interpolated from the straight line

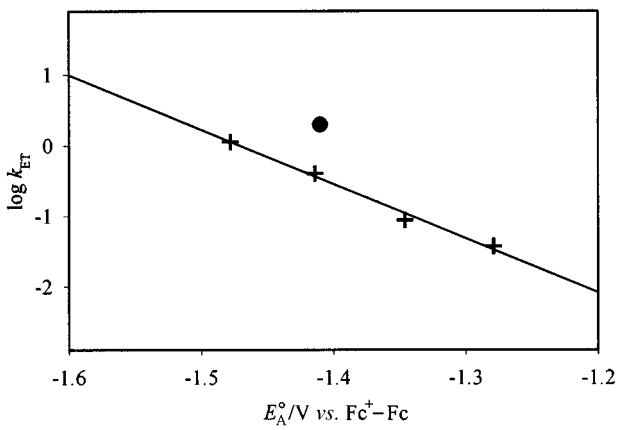

Fig. 2 Electron transfer rate constants (+) for the reaction between radical anions of aromatic compounds (2,3-dimethylanthraquinone, anthraquinone, 2,3-dimethylnaphthoquinone and 1,2-benzanthraquinone) and benzyl bromide as well as the rate constant (●) of the reaction between SmI_2 and benzyl bromide in THF–0.2 M NBu_4PF_6–0.02 M NBu_4I.

through the four points determined by linear least square analysis. Included in Fig. 2 is the rate constant k_{obs} of the reaction between SmI_2 and benzyl bromide (= 2.0 $dm^3\ mol^{-1}\ s^{-1}$) with a position slightly above the line. The value of k_{obs}/k_{ET} thus obtained is 5.9 which indicates that the electron transfer process does have inner-sphere character. Nevertheless, the ratio is relatively small and it suggests that the electronic interaction between SmI_2 and benzyl bromide in the transition state amounts to only a few kcal mol^{-1}.‖

As a representative for the class of carbonyl compounds, which are involved in many SmI_2-induced electron transfer reactions, we studied the reduction of acetophenone. For SmI_2 the reaction leads to the formation of a metal-complexed ketyl radical in the rate-controlling step. However, the procedure used for measuring k_{ET} for benzyl bromide can not be employed in this case since the electron transfer from aromatic radical anions to acetophenone, forming its radical anion, involves an energetically unfavourable equilibrium reaction. Still, the rate constant for the electron transfer process between an outer-sphere donor of $E^\circ = -1.41$ V and acetophenone can be estimated on the basis of the equations of Marcus and Eyring (using a collision frequency of $3 \times 10^{11}\ dm^3\ mol^{-1}\ s^{-1}$).[11] The E° of acetophenone is −2.52 V as measured by cyclic voltammetry, and if the reorganization energy of the reaction is assumed to be in the range 20–30 kcal mol^{-1}, k_{ET} can be calculated as *ca.* $10^{-8}\ dm^3\ mol^{-1}\ s^{-1}$. The rate constant k_{obs} for the reaction between SmI_2 and acetophenone was measured¶ to be 7 $dm^3\ mol^{-1}\ s^{-1}$ so in this case k_{obs}/k_{ET} approaches 10^9. This is a substantial value compared with the result for benzyl bromide and the mechanism in this case clearly can be classified as an inner-sphere electron transfer process with a strong electronic interaction in the transition state.

In conclusion, we provide the E° value for the SmI_2^+–SmI_2 couple in THF, and apply it to describe the mechanism of electron transfer from SmI_2 to two organic substrates. We are currently using the above methodology to investigate the mechanism of SmI_2-based reductions of other functionalities.

Notes and references

† Shabangi and Flowers recently measured the oxidation potential of SmI_2 in THF–0.1 M NBu_4PF_6 but did not investigate the mechanism of the electrode reaction nor its thermodynamic significance (ref. 5). The peak potential was −1.33 V *vs.* Ag–$AgNO_3$ (−1.21 V *vs.* Fc^+–Fc) at a sweep rate of 0.1 V s^{-1}.

‡ The experimental set-up for the electrochemical experiments was as described in ref. 6. The working electrode was a glassy carbon disk of diameter 1 mm. All potentials were reported *vs.* the ferrocenium–ferrocene (Fc^+–Fc) redox couple, the potential of which was measured to 0.52 V *vs.* SCE in THF–0.2 M NBu_4PF_6. Experiments were carried out at 20 °C. NBu_4I was added to the cell in order to suppress any ligand-exchange of I^- by PF_6^- in either SmI_2 or SmI_3. UV-spectral investigations revealed that at least 10 mM of NBu_4I must be present in the electrolyte solution (THF–0.2 M NBu_4PF_6) for the UV-spectrum to resemble that of SmI_2 or SmI_3 in THF alone. The upper concentration limit of NBu_4I was 30 mM, set by its solubility.

§ Digisim 2.1 software (Bioanalytical Systems Inc) was used for digital simulation. The diffusion coefficients of SmI_2 and SmI_2^+, *D*, were assumed to be equal. In the experiments, variation of the NBu_4I concentration in the range 10–30 mM had no detectable effect on the position of the peak potentials. This was attributed to the small dissociation constant of NBu_4I in THF ($\approx 10^{-6}$ mol dm^{-3})[7] and the resulting low concentration of free iodide. The concentration of iodide was assumed to be reasonably constant throughout the whole scan range due to the equilibrium reaction with NBu_4I and thus included in the forward rate constant k_f in the simulations. At lower concentrations of NBu_4I the cyclic voltammetric waves were shifted in a positive direction though being complicated by ligand exchange reactions involving PF_6^- from NBu_4PF_6.

¶ The reaction kinetics was followed by UV–VIS spectroscopy using a dip-probe technique (ref. 9). The decay of SmI_2 in the presence of a substrate was detected at 560 and 620 nm. No build-up of intermediates during the reaction could be detected in the wavelength range 300–800 nm. The presence of supporting electrolyte had no influence on the reaction rate. The kinetics for benzyl bromide and acetophenone followed the same rate law described by: $d[SmI_2]/dt = -nk_{obs}[SmI_2][substrate]$, where $n = 2$ for benzyl bromide and $n = 1$ for acetophenone. k_{obs} was determined under pseudo-first-order conditions using an excess of substrate.

‖ This is true even if one takes into account that the k_{obs}/k_{ET} ratio obtained should be considered as a minimum value;[10] the self-exchange reorganisation energy of the SmI_2^+–SmI_2 couple is somewhat higher than for the aromatic radical anions as indicated by the relatively low value of k° measured by cyclic voltammetry.

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