

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

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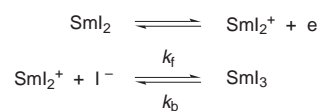
From the measured value of  $E^\circ$  ( $\text{SmI}_2^+/\text{SmI}_2$ ) in THF and using free energy plots, the electron transfer between samarium diiodide and acetophenone was shown to be clearly of inner-sphere nature; on the other hand, with benzyl bromide it is closer to an outer-sphere process.

Twenty years have almost passed since the first introduction of samarium diiodide ( $\text{SmI}_2$ ) as a reagent for organic synthesis by Kagan and coworkers.<sup>1</sup> 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.<sup>2</sup> 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  $\text{Sm(II)}$  and organic substrates.<sup>3</sup> In this paper, we describe the nature of the electron transfer between  $\text{SmI}_2$  and two substrates, namely benzyl bromide and acetophenone.

Paramount for the comprehension of electron transfer processes involving  $\text{SmI}_2$ , is that the standard potential of the  $\text{SmI}_2^+/\text{SmI}_2$  couple in THF be well defined. It is noteworthy that these fundamental measurements have not been performed even after 20 years of existence of  $\text{SmI}_2$  in the organic chemistry community. The potential cited today by organic chemists for the  $\text{Sm(III)}-\text{Sm(II)}$  couple of  $-1.80$  V vs. SCE was determined in 1948 by polarographic measurements in water,<sup>4</sup> which is simply not compatible with current studies.<sup>†</sup>

Hence, we set out to investigate the redox properties of  $\text{SmI}_2$  and  $\text{SmI}_3$  by means of cyclic voltammetry in a supporting electrolyte solution of  $\text{NBu}_4\text{I}$  (0.02 M) and  $\text{NBu}_4\text{PF}_6$  (0.2 M) in THF.<sup>‡</sup> Fig. 1 shows three of the voltammograms recorded for  $\text{SmI}_2$  at different sweep rates  $\nu$  in the range  $0.02\text{--}0.5$  V  $\text{s}^{-1}$ . The peak separation increases from ca. 150 to 300 mV as a function of  $\nu$ . As the peak potentials and currents acquired in the

voltammograms of  $\text{SmI}_2$  are in good agreement with the corresponding values obtained for  $\text{SmI}_3$ , 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  $\text{SmI}_2^+$  coordinates strongly with  $\text{I}^-$  present in the electrolyte solution.



Scheme 1

In order to determine the standard potential (or more correctly the formal potential)  $E^\circ$  of  $\text{SmI}_2^+/\text{SmI}_2$  from the cyclic voltammograms, the association constant ( $K = k_f/k_b$ ) for  $\text{SmI}_3$  is required. A rough estimate of  $K \approx 10^7$   $\text{dm}^3 \text{mol}^{-1}$  could be obtained simply by comparing conductivity measurements performed on  $\text{SmI}_3$  and  $\text{NBu}_4\text{I}$  in THF since the association constant for  $\text{NBu}_4\text{I}$  in THF has been estimated previously.<sup>7</sup> 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  $K[\text{I}^-]$ , digital simulations of the voltammograms (see Fig. 1) were carried out on the basis of the above reaction scheme.<sup>§</sup> Simulations revealed that  $K[\text{I}^-]$  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  $\nu$ . This led to a value for  $E^\circ$  of  $-1.41 \pm 0.08$  V vs.  $\text{Fc}^+/\text{Fc}$  and for the logarithm of the standard heterogeneous rate constant  $k^\circ$  (in  $\text{cm s}^{-1}$ ) of  $-2.20 \pm 0.70$ . Comparing these values of  $E^\circ$  and  $\log k^\circ$  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  $\text{SmI}_2$  towards a given substrate can now be assessed by comparing the reactivity of  $\text{SmI}_2$  and a corresponding outer-sphere electron donor.<sup>8</sup> In this way the degree of electronic interaction between  $\text{SmI}_2$  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  $E^\circ_{\text{A}}$  close to that of  $\text{SmI}_2^+$ .<sup>8</sup> The rate constants  $k_{\text{ET}}$  for the electron transfer reactions between the radical anions and benzyl bromide were measured<sup>¶</sup> and depicted in free energy plots of  $\log k_{\text{ET}}$  vs.  $E^\circ_{\text{A}}$  (Fig. 2). The value of  $k_{\text{ET}}$  ( $= 0.34 \text{ dm}^3 \text{mol}^{-1} \text{ s}^{-1}$ ) corresponding to the  $E^\circ$  of  $\text{SmI}_2^+ = -1.41$  V can be interpolated from the straight line

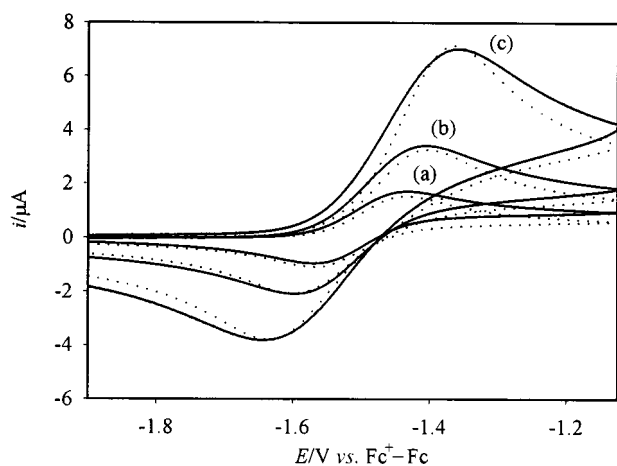
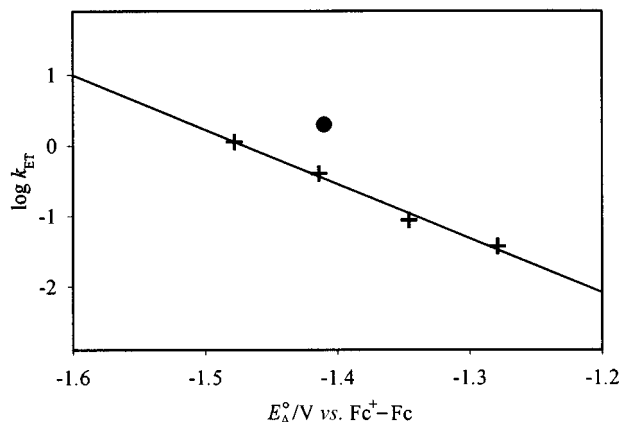


Fig. 1 Cyclic voltammograms of 2.5 mM  $\text{SmI}_2$  recorded in THF-0.2 M  $\text{NBu}_4\text{PF}_6$  + 0.02 M  $\text{NBu}_4\text{I}$  at a glassy carbon electrode (diameter = 1 mm) at sweep rates of (a) 0.02, (b) 0.1 and (c) 0.5 V  $\text{s}^{-1}$ . The dotted curves represent simulated curves based on the following parameters:  $E^\circ = -1.41$  V,  $k_f[\text{I}^-] = 1.5 \times 10^5 \text{ s}^{-1}$ ,  $k_b = 3.8 \times 10^3 \text{ s}^{-1}$ ,  $k^\circ = 0.0065 \text{ cm s}^{-1}$ ,  $D = 5.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , transfer coefficient  $\alpha = 0.5$  and capacitance  $C_d = 10^{-7}$  F.



**Fig. 2** Electron transfer rate constants (+) for the reaction between radical anions of aromatic compounds (2,3-dimethylantraquinone, anthraquinone, 2,3-dimethylnaphthoquinone and 1,2-benzanthraquinone) and benzyl bromide as well as the rate constant (●) of the reaction between SmI<sub>2</sub> and benzyl bromide in THF–0.2 M NBu<sub>4</sub>PF<sub>6</sub>–0.02 M NBu<sub>4</sub>I.

through the four points determined by linear least square analysis. Included in Fig. 2 is the rate constant  $k_{\text{obs}}$  of the reaction between SmI<sub>2</sub> and benzyl bromide ( $= 2.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) with a position slightly above the line. The value of  $k_{\text{obs}}/k_{\text{ET}}$  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<sub>2</sub> and benzyl bromide in the transition state amounts to only a few kcal mol<sup>-1</sup>.<sup>||</sup>

As a representative for the class of carbonyl compounds, which are involved in many SmI<sub>2</sub>-induced electron transfer reactions, we studied the reduction of acetophenone. For SmI<sub>2</sub> the reaction leads to the formation of a metal-complexed ketyl radical in the rate-controlling step. However, the procedure used for measuring  $k_{\text{ET}}$  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  $E^\circ = -1.41 \text{ V}$  and acetophenone can be estimated on the basis of the equations of Marcus and Eyring (using a collision frequency of  $3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).<sup>11</sup> The  $E^\circ$  of acetophenone is  $-2.52 \text{ V}$  as measured by cyclic voltammetry, and if the reorganization energy of the reaction is assumed to be in the range 20–30 kcal mol<sup>-1</sup>,  $k_{\text{ET}}$  can be calculated as *ca.*  $10^{-8} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The rate constant  $k_{\text{obs}}$  for the reaction between SmI<sub>2</sub> and acetophenone was measured<sup>¶</sup> to be  $7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  so in this case  $k_{\text{obs}}/k_{\text{ET}}$  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  $E^\circ$  value for the SmI<sub>2</sub><sup>+</sup>–SmI<sub>2</sub> couple in THF, and apply it to describe the mechanism of electron transfer from SmI<sub>2</sub> to two organic substrates. We are currently using the above methodology to investigate the mechanism of SmI<sub>2</sub>-based reductions of other functionalities.

## Notes and references

† Shabangi and Flowers recently measured the oxidation potential of SmI<sub>2</sub> in THF–0.1 M NBu<sub>4</sub>PF<sub>6</sub> but did not investigate the mechanism of the

electrode reaction nor its thermodynamic significance (ref. 5). The peak potential was  $-1.33 \text{ V vs. Ag–AgNO}_3$  ( $-1.21 \text{ V vs. Fc}^+/\text{Fc}$ ) at a sweep rate of  $0.1 \text{ V s}^{-1}$ .

‡ 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<sup>+</sup>–Fc) redox couple, the potential of which was measured to  $0.52 \text{ V vs. SCE}$  in THF–0.2 M NBu<sub>4</sub>PF<sub>6</sub>. Experiments were carried out at  $20^\circ \text{C}$ . NBu<sub>4</sub>I was added to the cell in order to suppress any ligand-exchange of I<sup>-</sup> by PF<sub>6</sub><sup>-</sup> in either SmI<sub>2</sub> or SmI<sub>3</sub>. UV-spectral investigations revealed that at least 10 mM of NBu<sub>4</sub>I must be present in the electrolyte solution (THF–0.2 M NBu<sub>4</sub>PF<sub>6</sub>) for the UV-spectrum to resemble that of SmI<sub>2</sub> or SmI<sub>3</sub> in THF alone. The upper concentration limit of NBu<sub>4</sub>I was 30 mM, set by its solubility.

§ Digisim 2.1 software (Bioanalytical Systems Inc) was used for digital simulation. The diffusion coefficients of SmI<sub>2</sub> and SmI<sub>2</sub><sup>+</sup>,  $D$ , were assumed to be equal. In the experiments, variation of the NBu<sub>4</sub>I 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<sub>4</sub>I in THF ( $\approx 10^{-6} \text{ mol dm}^{-3}$ )<sup>7</sup> 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<sub>4</sub>I and thus included in the forward rate constant  $k_f$  in the simulations. At lower concentrations of NBu<sub>4</sub>I the cyclic voltammetric waves were shifted in a positive direction though being complicated by ligand exchange reactions involving PF<sub>6</sub><sup>-</sup> from NBu<sub>4</sub>PF<sub>6</sub>.

¶ The reaction kinetics was followed by UV–VIS spectroscopy using a dip-probe technique (ref. 9). The decay of SmI<sub>2</sub> 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:  $d[\text{SmI}_2]/dt = -nk_{\text{obs}}[\text{SmI}_2][\text{substrate}]$ , where  $n = 2$  for benzyl bromide and  $n = 1$  for acetophenone.  $k_{\text{obs}}$  was determined under pseudo-first-order conditions using an excess of substrate.

|| This is true even if one takes into account that the  $k_{\text{obs}}/k_{\text{ET}}$  ratio obtained should be considered as a minimum value;<sup>10</sup> the self-exchange reorganisation energy of the SmI<sub>2</sub><sup>+</sup>–SmI<sub>2</sub> couple is somewhat higher than for the aromatic radical anions as indicated by the relatively low value of  $k^\circ$  measured by cyclic voltammetry.

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