

Quantifying the Electrostatic Driving  
Force behind SmI<sub>2</sub> Reductions

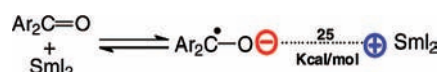
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## ABSTRACT



The equilibrium constant for the electron transfer between SmI<sub>2</sub> and substituted benzophenones was determined. The electron transfer reactions are exothermic with  $\Delta G_{\text{eq}}$  ranging from  $-5.1$  to  $-1.6$  kcal/mol. Redox potentials suggest that the electron transfer reactions should be endothermic by ca. 25 kcal/mol, contrary to the experimental observation. It is suggested that the change from endothermicity to exothermicity stems from the electrostatic attraction between the negatively charged radical anion and Sm<sup>3+</sup>.

A recent review by Kagan<sup>1</sup> demonstrated that since the discovery of SmI<sub>2</sub> in 1979<sup>2</sup> its use in organic chemistry has increased substantially. One of the most common reactions for which this single electron transfer agent is employed is the reduction of carbonyl compounds. In fact, going over the reviews published in recent years<sup>1,3</sup> on the chemistry of SmI<sub>2</sub>, one can hardly encounter a reaction where one of the reactants lacks a carbonyl function. The rates of these reactions are very dependent on the reduction potential of the carbonyl moiety. Thus, aliphatic aldehydes and ketones having low reduction potentials react relatively slowly<sup>4</sup> with SmI<sub>2</sub>, whereas aromatic ketones react much faster.<sup>5</sup> In this communication we show that the electrostatic interaction within the ion pair generated by the electron transfer provides the energy to transform the electron transfer process from being highly endothermic to being exothermic.

The electron transfer step in the SmI<sub>2</sub> reductions of various substituted benzophenones used in the present study (eq 1) was found to occur in less than 2 ms (the mixing dead time in the stopped-flow spectrophotometer).

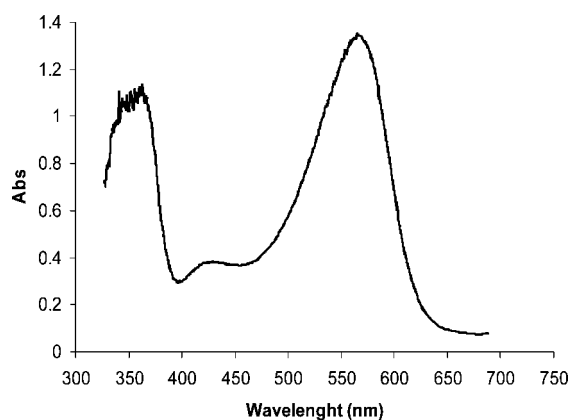
DCl; Ar<sub>1</sub> = Ar<sub>2</sub> = p-ClC<sub>6</sub>H<sub>4</sub>H; Ar<sub>1</sub> = Ar<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>DMe; Ar<sub>1</sub> = Ar<sub>2</sub> = p-MeC<sub>6</sub>H<sub>4</sub>DA; Ar<sub>1</sub> = Ar<sub>2</sub> = p-MeOC<sub>6</sub>H<sub>4</sub>DMA; Ar<sub>1</sub> = p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; Ar<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>

In Figure 1 we present the spectrum obtained immediately after the mixing of benzophenone with SmI<sub>2</sub>. The spectrum of the free radical anion in DMF has been reported to have a  $\lambda_{\text{max}}$  of ca. 754nm,<sup>6</sup> unlike the maximum in Figure 1. The present spectrum was found to be similar to that of a solution of benzophenone and sodium, commonly used for the drying of THF where the sodium cation is paired to the radical anion (see Figure S1, Supporting Information). We therefore conclude that the spectrum shown in Figure 1 is that of the radical anion of benzophenone paired to the Sm<sup>3+</sup>.

The slow subsequent coupling of the generated radical anions to the corresponding pinacol products (eq 2) enabled

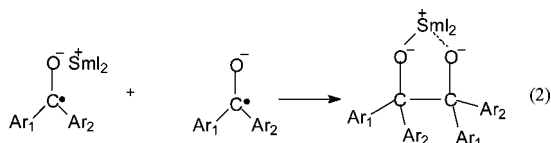
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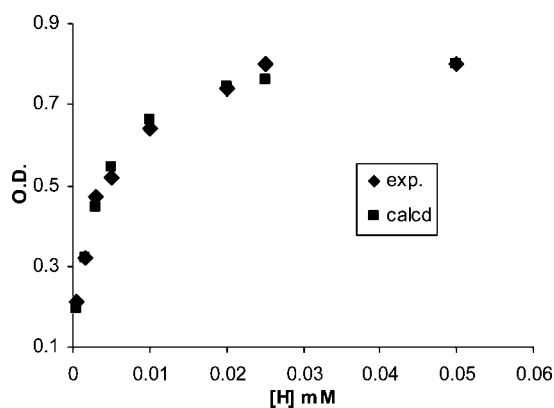


**Figure 1.** UV-vis spectrum of the radical anion of benzophenone generated with  $\text{SmI}_2$ .

us to measure, for the first time, the equilibrium constant for the electron transfer reaction between  $\text{SmI}_2$  and a series of substituted benzophenones.



The determination of the equilibrium constants was performed in the following manner: the concentration of the ketone was increased until the absorption at the  $\lambda_{\text{max}}$  of the radical anion reached a plateau from which the extinction coefficient ( $\epsilon$ ) of the radical anions was determined. The equilibrium constants were calculated using the “solver” function in Excel for data fitting (Figure 2 and Figures



**Figure 2.** Absorption as a function of the concentration of benzophenone with 1.25 mM  $\text{SmI}_2$  in THF.

S2–S5, Supporting Information). Each experiment was repeated three times, and experimental error was  $\pm 4\%$ .

Due to substrate solubility problems, the fit for **DA** is of lower quality than that of the other substrates. In control

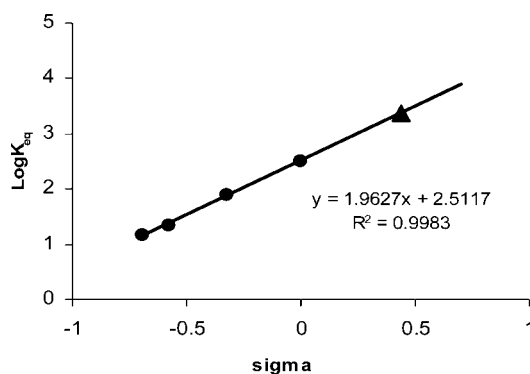
experiments where the  $\text{SmI}_2$  concentration was varied over the range 1.25–10 mM and the concentration of the substrates **H**, **DA**, and **DMe** was kept constant (20 and 50 mM), the same equilibrium constants ( $\pm 4\%$ ) were obtained. This conforms with the known monomeric nature of  $\text{SmI}_2$  in THF.<sup>7</sup> The only substrate that even at its lowest concentrations completely oxidized all of the  $\text{SmI}_2$  was **DCI**.

The  $\lambda_{\text{max}}$ , the extinction coefficients, the equilibrium constants ( $K_{\text{eq}}$ ) and the corresponding equilibrium free energies ( $\Delta G_{\text{eq}} = -RT \ln K_{\text{eq}}$ ) for the various substituted benzophenones are given in Table 1.

**Table 1.** Spectral, Equilibrium Constant, and Free Energy Data for the Radical Anions of Substituted Benzophenones

X	$\lambda_{\text{max}}$ ( $\epsilon$ )	$K_{\text{eq}}$ ( $\text{M}^{-1}$ )	$\Delta G_{\text{eq}}$ (kcal/mol)
<b>DCI</b>	590 (3860)	2373	−4.7
<b>H</b>	572 (4470)	321	−3.5
<b>DMe</b>	579 (3980)	80	−2.6
<b>DA</b>	578 (1560)	21.9	−1.85
<b>DMA</b>	588 (2000)	15	−1.6

The equilibrium constant for **DCI** was obtained by extrapolation of the plot of  $\log K_{\text{eq}}$  versus the Hammett constant<sup>8</sup>  $\sigma$  (Figure 3).



**Figure 3.** Hammett plot for the equilibrium constant for the electron transfer from  $\text{SmI}_2$  to the substituted benzophenones. The triangle is the extrapolated value for *p,p*-dichlorobenzophenone.

We now compare these  $\Delta G_{\text{eq}}$  values with the  $\Delta G$  obtained from the differences in the reduction potentials of the substituted benzophenones and  $\text{SmI}_2$  ( $\Delta G_{\text{rd-ox}}$ ). The reduction potentials of the substituted benzophenones in  $\text{CH}_3\text{CN}$  versus SCE are given in Table 2.<sup>9</sup> In this work we have determined the reduction potentials of substituted benzophenones in THF

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**Table 2.** Electrochemical Data and  $\Delta\Delta G$  Values for the Electron Transfer to Substituted Benzophenones<sup>a</sup>

X	$E_{1/2}^{\text{red}}$ (eV)	$\Delta G_{\text{rd-ox}}$ (kcal/mol)	$\Delta\Delta G$ (kcal/mol)
<b>DCI</b>	-1.67	18.0	22.7
<b>H</b>	-1.83	21.8	25.2
<b>DMe</b>	-1.95	24.4	27.0
<b>DA</b>	-2.02	26	27.9
<b>DMA</b>	-2.14	28.8	30.4

<sup>a</sup> Redox values versus SCE for the substituted benzophenones are in CH<sub>3</sub>CN and that for SmI<sub>2</sub><sup>13</sup> is in THF.

by means of cyclic voltammetry versus a Ag/AgNO<sub>3</sub> electrode. The working electrode was Pt, and tetrabutylammonium hexafluorophosphate at a concentration of 0.2 M was employed as an electrolyte (we were unsuccessful in determining the values for **DCI**). Table 3 presents the results

**Table 3.** Electrochemical Data and  $\Delta\Delta G$  Values for the Electron Transfer to Substituted Benzophenones (in THF)

X	$E_{1/2}^{\text{red}}$ (eV)	$\Delta G_{\text{rd-ox}}$ (kcal/mol)	$\Delta\Delta G$ (kcal/mol)
<b>H</b>	-2.03	15.6	19.1
<b>DMe</b>	-2.15	18.5	21.1
<b>DA</b>	-2.37	23.5	25.3
<b>DMA</b>	-2.5	26.4	28

of this cyclic voltammetry analysis. The redox potential of SmI<sub>2</sub> in THF versus Ag/AgNO<sub>3</sub> is -1.36V.<sup>10</sup> Listed in Table 2 are the  $\Delta G_{\text{rd-ox}}$  values for the equilibrium constants using the reduction potential of SmI<sub>2</sub> in THF as well as the difference ( $\Delta\Delta G$ ) between  $\Delta G_{\text{eq}}$  and  $\Delta G_{\text{rd-ox}}$  in CH<sub>3</sub>CN. Table 3 presents the data for THF.

The two sets of data reveal a most surprising result, namely, that the redox potentials not only predict that the electron transfer should be highly endothermic whereas the actual electron transfer is exothermic, but also that there is, on the average, a large gap of ca. 25 kcal/mol between the experimentally determined  $\Delta G_{\text{eq}}$  and the electrochemically determined  $\Delta G_{\text{rd-ox}}$  (last column, Tables 2 and 3). *Bridging this energy gap is, most probably, the Coulombic interaction between the negatively charged radical anion and the Sm<sup>+3</sup> ion.* As can be seen from the data given in Tables 2 and 3, the electrostatic stabilization is larger for the electron-donating substituents than for the other derivatives. This

(10) Literature value, -1.33V; see: Shabangi, M.; Flowers, R. A. *Tetrahedron Lett.* **1997**, 38, 1137–1140.

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suggests that although the charge in the radical anion is delocalized over the whole molecule, the main interaction of the Sm<sup>3+</sup> is with the oxygen atom to which the electron donating substituents are “pushing” the negative charge. DFT calculations using CHELPG at the B3LYP/6-31+G\* level<sup>11</sup> show that the negative charge on oxygen increases from 0.61 for **DCI** to 0.66 for **DMA** (see Supporting Information).

The issue of inner versus outer sphere electron transfer in the reactions of SmI<sub>2</sub> was the subject of several papers.<sup>5c,12,13</sup> The data above clearly support the notion that for carbonyl compounds, SmI<sub>2</sub> works by an inner sphere electron transfer mechanism. As data presented above show, an outer sphere electron transfer, lacking the Coulombic interaction, would be highly endothermic.

The effect of ion pairing on the kinetics and thermodynamics of chemical processes is overwhelmingly documented in the old as well as in the new literature.<sup>14</sup> Moreover, the effect of the interaction of various cations with neutral substrates on the reduction potential of these substrates was thoroughly studied.<sup>15</sup> Flowers had demonstrated that inner sphere accessibility is of paramount importance.<sup>16</sup> However, to the best of our knowledge, this is the first time that the contribution of the electrostatic interaction<sup>17</sup> to an electron transfer process within a pair of reacting species, has been quantitatively assessed. We have shown that contrary to common assumption, the redox potential, although very important, is not the sole player to be considered. A Coulombic interaction energy of 25 kcal/mol, as found in the present case, amounts to nearly 20 orders of magnitude in equilibrium or rate constants. Because of this enormous effect, parameters affecting the electrostatic interaction, such as the hardness and softness of the generated charged species as well as their interaction with the reaction medium, will also significantly affect any chemical reaction in which opposite charges are generated.

**Supporting Information Available:** Figures S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Throughout this paper we have liberally used the term electrostatic interaction. However, this interaction may be also partly covalent.