Reductions with SmI_2: mechanistic probe for distinguishing between two operational modes of proton transfer†

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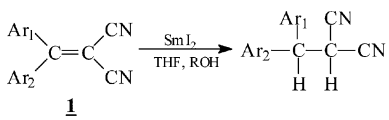
The reduction of 1,1-diaryl-2,2-dicyanoethylenes with SmI_2 in THF was studied in the presence of four proton donors: H_2O, MeOH, i-PrOH and trifluoroethanol (TFE). The kinetic order for the first two is nearly unity at low proton donor concentrations and approaches four at high concentrations, whereas, for i-PrOH and TFE, the log–log plot is linear with a slope smaller than one. Detailed analysis shows that a curved log–log plot such as for H_2O and MeOH is indicative of a major contribution by protonation within an ion pair of the radical anion and Sm^{+3} complexed to a variable number of proton donor molecules, whereas a linear plot is a result of protonation from the bulk solution.

Introduction

Proton donors are crucial in most reduction reactions. In the case of SmI_2,[1] proton donors may have a dramatic effect on the course of the reaction as well as on its rate. In the traditional sequence of electron–proton–electron–proton transfer steps, the kinetic order in the proton donor may be first or second depending on the identity of the rate determining step. However, a variety of kinetic orders have been reported in the literature. For example, in the reduction of acetophenone, the kinetic order for H_2O was found to vary from 1 to 2, and for MeOH from 1 to 1.3 as the concentration of the proton donor increased, while for EtOH and trifluoroethanol (TFE) the kinetic order remained 1.[2] In all these cases the kinetic H/D isotope effect was *ca.* 2, showing that protonation took place in the rate determining step.

In a previous work[3] we have shown that a shortage of the reducing agent (SmI_2) leads to a biphasic reaction where the first step is a dimerization of the substrate 1.1-diaryl-2,2-dicyanoethylenes **1**. Herein we report on reactions (eqn 1) performed with a large excess of SmI_2 and focus on the unusual behavior of the proton donors H_2O, MeOH, i-PrOH and TFE.



(1)

$Ar_1 = C_6H_5$; Ar_2 = p-MeO-C_6H_4: **MA**

$Ar_1 = Ar_2$ = p-MeO-C_6H_4: **DA**

Results and discussion

The reactions were performed under pseudo first order conditions (*ca.* 30 fold excess of SmI_2) and were followed at the λ_{max} of the substrate in a stopped flow spectrophotometer. The pseudo first order rate constants are given in the tables below. The two substrates, **MA** and **DA**, were chosen because the electron donating substituents slow the reactions to the extent that reliable monitoring of the kinetics is possible. Although the radical anions of the substrates were formed during the dead time of the mixing, spectral analysis showed that at the low concentrations used (typically, [substrate] = 0.1 mM; [SmI_2] = 2.5 mM), only about two thirds of the substrate was converted into its radical anion. The reaction order in SmI_2 was found to be about 1.7 (Table 1; Fig. 1).

Table 1 Pseudo first order rate constants for the reaction of **DA** (0.05 mM) in the presence of 0.5 M MeOH as a function of SmI_2 concentration

[SmI_2]/mM	k/s^{-1}
1.5	2.57
3	9.65
6	27.5
9	53.5

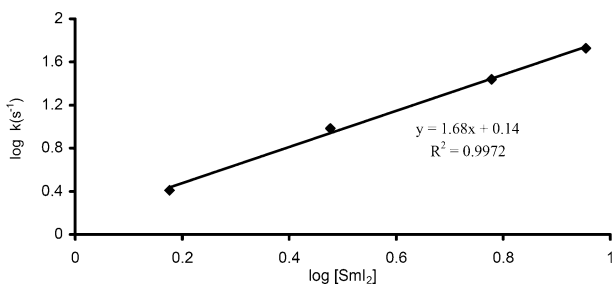


Fig. 1 A log–log plot of the first order rate constants for the reaction of **DA** (0.05 M) in the presence of 0.5 M MeOH as a function of SmI_2 concentration.

This fractional order in the SmI_2 can be easily rationalized. The overall reduction necessitates two electrons. Had the substrate been completely converted into its radical anion at the mixing stage then the kinetics of the reaction would have involved only one electron transfer step (that of the second electron) rendering the kinetics to be first order for the SmI_2. A second order for SmI_2 would have been observed if the first electron transfer of the

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reaction had taken place after the mixing time and was part of the monitored kinetics. Since the radical anion is only *partly* formed in a rapid equilibrium established at the dead time of the mixing, the kinetic order for SmI_2 is intermediate between one and two.

Pseudo first order rate constants as a function of TFE and MeOH concentrations are given in Table 2. The corresponding data for **DA** with H_2O and **MA** with i-PrOH are given in Tables 3 and 4 respectively. The kinetic isotope effect MeOH/MeOD was determined for **MA** and was found to be 1.05 ± 0.06 (average of four experiments).

The data clearly show that the rate dependence on the proton donor follows the order H_2O > MeOH > TFE > i-PrOH. This order is neither in accord with their effect on the polarity of the THF solution as measured by ET30 values[4] (see Table S1 and Fig. S1†) nor with their acidity order.[5]

Based on their kinetic behavior, the four proton donors could be divided into two groups, TFE and i-PrOH on the one hand, and H_2O and MeOH on the other.

The common feature shared by i-PrOH and TFE is a linear dependence of the first order rate constants on the proton donor concentration in a log–log plot (Fig. 2 and 3). On the other hand, the characteristic feature of H_2O and MeOH is a variable order in the proton donor. Namely, the log–log plots are curved as shown in the figures. In the log–log plot for **DA** reduction (Fig. 1), at low MeOH concentrations (30–60 mM) the order in MeOH is 0.88 and it increases to 3.6 at the high range of MeOH concentration (0.5–1 M). Similarly, with H_2O, at the lower concentration range (1–3 mM) the order in water is 1.0 and it increases to 3.95 at the higher end of the range (16–33 mM).

Table 2 First order rate constants as a function of alcohol concentration for the reactions of **DA** and **MA** with TFE and MeOH ([SmI_2] = 3 mM; [substrate] = 0.1 mM])

	k/s^{-1}	
[TFE]/M	**DA**	**MA**
0.25	0.049	8.1
0.5	0.069	12
1	0.12	22
2	0.23	34
[MeOH]/M	**DA**	**MA**
0.0313	0.055	8
0.0625	0.1	15
0.125	0.3	43
0.25	1.7	160
0.5	17	
1	200	

Table 3 First order rate constants for the reaction of **DA** (0.1 mM) as a function of water concentration ([SmI_2] = 3 mM)

[H_2O]/mM	k/s^{-1}
1	0.017
2.95	0.052
4.9	0.12
8.81	0.52
16.63	5.2
32.25	71

Table 4 First order rate constants for the reaction of **MA** (0.1 mM) as a function of i-PrOH concentration ([SmI_2] = 3 mM)

[i-PrOH]/M	k/s^{-1}
0.25	5.2
0.5	7.3
1	11
2	19

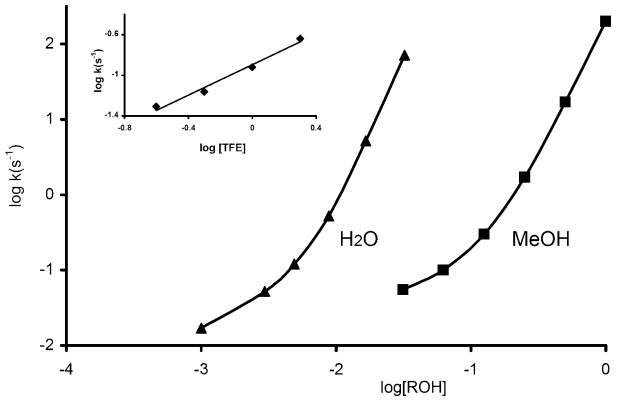

Fig. 2 A log–log plot of the first order rate constants for the reaction of **DA** (0.01 M) with SmI_2 (3mM) as a function of ROH concentration. In the inset, the data for the reaction with TFE is shown.

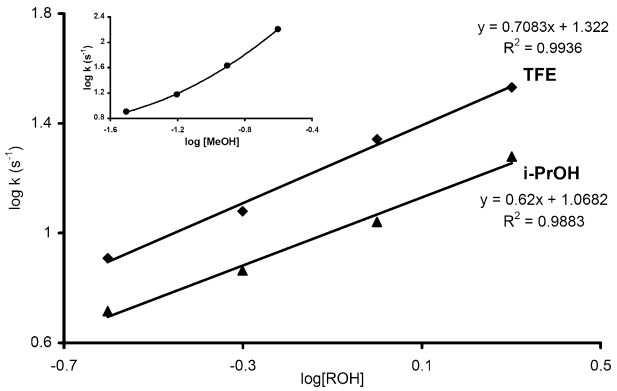

Fig. 3 A log–log plot of the first order rate constants for the reaction of **MA** (0.01 M) with SmI_2 (3mM) as a function of ROH concentration. In the inset, the data for the reaction with MeOH is shown.

The dichotomous behavior can be attributed to two different modes of protonation: a-protonation by proton donors present in the bulk of the solution and b-protonation by proton donors complexed to the SmI_2. We have shown that MeOH complexes to SmI_2.[6] Recently, Prasad and Flowers have shown[7] that water forms a complex with SmI_2. They also noted that at concentrations of water much higher than used here, SmI_2 dimerizes. The formation of such complexes is manifested as a change in the spectrum of SmI_2. Unlike MeOH and H_2O, addition of i-PrOH or TFE (up to 1 M) to a THF solution of SmI_2 did not cause any change in the spectrum of the SmI_2 present in the solution. The above clearly suggests that the alcohols i-PrOH and TFE react from the bulk whereas MeOH and H_2O react from their complex to SmI_2.

It is reasonable to assume that at low ligand (MeOH and H_2O) concentration, only partial complexation takes place. Namely, the first SmI_2 complex to be formed has one ligand molecule. Then, as the concentration of the ligand in the solution is increased, the di, tri, tetra *etc.* coordinated SmI_2 complexes are formed. The

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different complexes do not necessarily have the same equilibrium constant (K) for their formation.[8] A slope of between 2 and 3 in the log–log plot for MeOH may for example suggest that the protonation is by $SmI_2(MeOH)_2$ and by $SmI_2(MeOH)_3$, and the actual slope reflects the relative population of these two complexes as well as their relative reactivities. Clearly, the same slope could be obtained by other combinations including protonation from the bulk combined with that from a complex.

The complexity of the kinetics of protonation from a complex between SmI_2 and the proton donor is nicely demonstrated as follows. We have simulated a case where SmI_2 forms complexes with one, two, three and four molecules of H_2O, each of them reacting with the substrate at slightly different rates, using the SPECFIT[9] program. The reaction scheme and the rate constants are given in the supporting information section (Table S2).† The log–log plot (Fig. 4) is sigmoidic. At low proton donor concentration the kinetic order (slope) in the proton donor is one. At high concentrations the graph levels off due to saturation and complete formation of the tetracoordinated SmI_2. In the middle zone, the slope approaches four. This is without considering any competing mechanism, such as dianion formation or protonation from the bulk, or that at high concentrations of proton donor, the protonation may be so fast as to render the previous step rate determining.

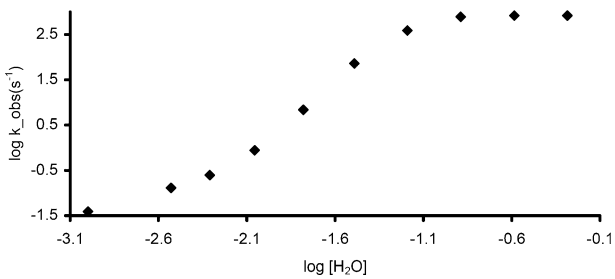
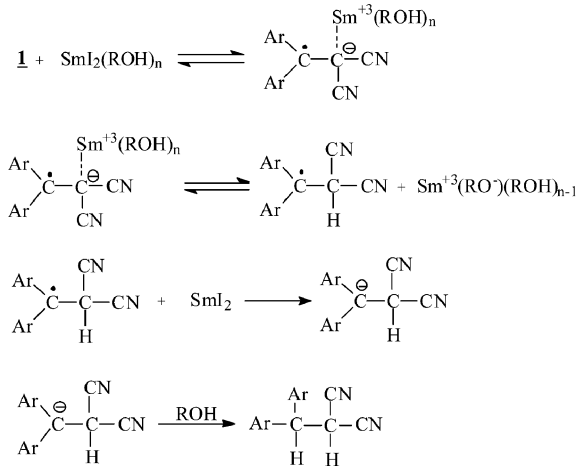


Fig. 4 A log–log plot for a simulation of protonation by H_2O from within four different complexes with SmI_2.

It should be pointed out that in principle, an order higher than four in these ligands could be achieved. However, at higher proton donor concentrations, the reactions became too fast to be measured. Thus, the order of nearly four observed at high MeOH and water concentration is not meant to imply that higher coordination numbers do not exist.

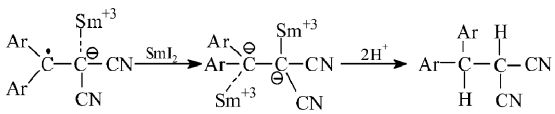
We now address the question: why is protonation from a complex more facile than protonation from the bulk? For this purpose let us focus on the region where the slope in the log–log plot is 2 (Fig. 2; [MeOH] ≈ 0.125 M) and for the sake of simplicity let us use as an example a situation where all the SmI_2 in the solution is ligated by two MeOH molecules. Under these conditions, the concentration of the protonating complex will be 0.003 M, whereas that of the free MeOH will be *ca.* 0.12 M. Namely, the concentration of $SmI_2(MeOH)_2$ is 40 times smaller than that of the free alcohol and yet, protonation occurs mainly from that complex. We think this is the result of two different factors. The first one stems from the fact that in THF, the radical anion and Sm^{+3} are highly paired. As a result, the effective molarity[10] of the complexed alcohol in the vicinity of the radical anion is very high relative to that in the bulk. This is in accordance with our previous finding that protonation occurs faster than ligand exchange.[6] Secondly, the complexation to the samarium drastically increases the acidity of the proton donor. Brown *et al.*[11] has shown that complexation to Eu^{+3} increases the acidity of MeOH by *ca.* 10 pK_a units. Assuming a similar effect with Sm^{+3}, this will reduce the pK_a of the complexed MeOH in THF to 19.[12]

The data could be accommodated by several mechanistic paths. However, the most plausible mechanism for MeOH and water as proton donors, considering the kinetic order in SmI_2 and the absence of isotope effect, is one in which the first proton is reversibly transferred within the complex between the radical anion and the ROH coordinated samarium to generate the radical at the benzylic position. This later on accepts an electron at a rate determining step from another SmI_2 with the final protonation in a post rate determining step (Scheme 1).



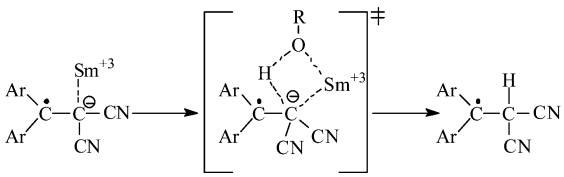
Scheme 1

Another important feature is the fractional order for the alcohols TFE and i-PrOH (0.6–0.75). One possible explanation is a reaction by a competing mechanism involving the formation of a dianion with the second electron transfer being the rate determining step (eqn 2).



(2)

Alternatively, TFE and i-PrOH may form a complex with the samarium which contains only one molecule of the alcohol (this may not result in any noticeable changes in the spectrum). In this case, depending on the concentration of alcohol used for the kinetic measurements, the order in the alcohol may vary between zero (at saturation—complete formation of the $SmI_2(ROH)$ complex) and one. Protonation by alcohol molecules of the bulk most probably takes place from the uncomplexed alcohol in a transition state where the incipient alkoxide ion is stabilized by the Sm^{+3} paired to the radical anion (eqn 3).



(3)

In conclusion, we have demonstrated that the two mechanistic options for protonation in the SmI_2 reaction are distinguishable

from their log–log plots. A curved log–log plot such as for H_2O and MeOH is indicative of a major contribution by protonation within an ion pair of the radical anion and Sm^{+3} complexed to a variable number of proton donor molecules, whereas a linear plot is a result of protonation from the bulk solution. It should be emphasized that in most cases, a kinetic study is limited to a relatively narrow range of reactant concentrations since at the lower end, the reaction may be too slow and at the other end it may be too fast to be measured. Fig. 4 shows that it is hazardous to derive conclusions from a narrow range of acquired data as in the parable of the "blind men and the elephant".

Experimental

THF was refluxed over Na wire with benzophenone and distilled under argon. Water content was determined (K. F. Coulometer 652) to be *ca.* 20 ppm. SmI_2 was diluted as needed from a 0.1 M commercial THF solution (actual concentration 0.08–0.09 M). The concentration of the SmI_2 solution was spectroscopically determined ($\lambda = 615$ nm; $\varepsilon = 635$). All the 1,1-diaryl-2,2-dicyanoethylenes used in the kinetic studies are known compounds.[3,6]

The kinetics of the reactions were followed using a stopped flow spectrophotometer (Hi-Tech SF-61DX2) in a glove box under a nitrogen atmosphere. The reactions were monitored at 340 and 350 nm for **DA** and **MA** respectively. The proton donor was mixed with the substrate solution. At the end of each series of kinetic measurements, the first measurement was repeated in order to ensure reproducibility within a set. The deviation did not usually exceed 8%. The kinetics were analyzed using KinetAsyst (v. 2.2, Hi-Tech Ltd.) and SPECFIT Global Analysis System (v. 2.11, Spectrum Software Associates).[9]

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