Rate Study of Proton Catalyzed Sml₂ Reduction of 2-Heptanone and 1,2-Epoxydecane

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Rate constants directly measured from the GC-analyzed method for SmI_2 reduction of 2-heptanone and 1,2-epoxydecane in the presence of various proton sources were obtained. Water exhibits much stronger catalytic effect than methanol and t-butanol. Dependence of reaction rates on concentration of SmI_2 and temperature were studied.

INTRODUCTION

There has been considerable progress over the last decade in the use of samarium diiodide in the syntheses of various organic compounds.^{1,2} In these reactions, HMPA was used as a powerful catalyst originally introduced by Inanaga^{1h} who observed that the reduction potential of SmI2 increases after the addition of HMPA to a THF solution of SmI₂. The X-ray structure of HMPA-coordinated SmI₂ complex³ showing four strong electron donating HMPA ligands to Sm(II) ion explains why the reducing power of SmI2 is greatly enhanced upon addition of HMPA. In our previous work, rate constants directly measured from the GC-analyzed method⁴ for HMPA catalyzed reduction of 2-haptanone⁵ and samarium Barbier reaction⁶ were obtained. In addition to HMPA, the proton also plays an important role for SmI2 reductions both in catalyzing the reactions and in producing specific products.^{1b} According to Hasegawa and Curran's report,1g water not only acted as a poor quenching reagent for SmI₂, but it actually accelerated SmI2 reduction after being added. We therefore study the catalytic effect of H₂O, CH₃OH and *t*-BuOH on SmI₂ reduction of 2-heptanone and 1,2-epoxydecane which are resistant to the action of SmI2 in the absence of a suitable additive. The absolute rate constants were obtained for these reactions.

RESULTS AND DISCUSSION

Pseudo-first-order electron transfer rate constants were obtained by plotting $log(C_t-C_{\infty})$ versus time for at least two half-lives. Here C_t and C_{∞} represent the concentrations of the substrates at time t and infinity, respectively. Fig. 1, for example, shows the plot for 2-heptanone. The first order rate of decay of 2-heptanone was also confirmed by applying different initial concentrations of this reactant (Table 1). On the other hand, we monitored the formation of reaction product, 2-

heptanol. The rate constants from these two approaches match perfectly (Table 2).

A series of 2-heptanone reduction reactions with different proton sources were carried out and the catalytic effect was examined (Table 3). The results show that water exhibits a much stronger accelerating effect than methanol and *t*-butanol. Since the alcohol-catalyzed reactions were quite slow, in order to obtain the rates in measurable time, higher temperature was needed. Owing to the tremendous amount of oxygen present in water and alcohols, we removed oxygen as much as possible by boiling these solvents then cooling them under nitrogen prior to use. However, the remaining oxygen is still effective in slowly destroying SmI₂. Therefore, the initial rates were taken under such a condition. According to data in Table 3, k_{ps} can be plotted against concentration of proton sources, such as that shown in Fig. 2., and normally k_{ps} reaches a limiting value as the concentration of proton source is raised to a



Fig. 1. Pseudo first-order rate plot of SmI₂ reduction of 2-heptanone; $[SmI_2] = 9.5 \times 10^{-2}$ M, $[t-BuOH] = 8.3 \times 10^{-2}$ M, $[2-heptanone]_0 = 2.0 \times 10^{-3}$ M, T = 25 °C.

[2-heptanone] ₀	k _{ps} , sec ⁻¹
$ \frac{4.0 \times 10^{-3}}{2.0 \times 10^{-3}} $	2.2×10^{-6} 2.3×10^{-6}
$a[SmI_2] = 9.4 \times 10^{-2} \text{ M;} [t-B]$	BuOH] = 8.3×10^{-2} M; T = 25 °C

Table 1.^a Dependence of Pseudo-first-order Rate Constants on Initial Concentration of Substrates

certain value. Therefore, the following relationship can be derived as

 $Rate_{t-Butanol} = k_1[t-BuOH][2-heptanone]$ $Rate_{Methanol} = k_2[CH_3OH][2-heptanone]$ $Rate_{Water} = k_3[H_2O][2-heptanone]$

for the linear part of these graphs, and the slopes obtained can be used to calculate k_1 , k_2 and k_3 which are dependent on [SmI₂] and temperature. Under our reaction condition, k_1 , k_2 , k_3 are approximated to be 7.8×10^{-5} , 1.1×10^{-4} , 5.1×10^{-4} , respectively.



Fig. 2. Dependence of t-butanol concentration on pseudo first-order rate constant. $[SmI_2] = 8.1 \times 10^{-2} \text{ M}, [2-\text{heptanone}]_0 = 2.0 \times 10^{-3} \text{ M}, T = 35 \text{ °C}.$

Table 2.^a Rates of Decay of 2-Heptanone and Formation of 2-Haptanol

k _D , sec ⁻¹		k _F , sec ⁻¹
2.3×10^{-6}		$2.2 imes 10^{-6}$
	2	2

^a [SmI₂] = 9.4×10^{-2} M; [*t*-BuOH] = 8.3×10^{-2} M; [2-heptanone]_o = 2.0×10^{-3} M; T = 25 °C. k_D and k_F represent pseudo-first-order rate constants of reactant decay and product formation, respectively.

 SmI_2 concentration dependence on reaction rates was studied in the presence of *t*-butanol in which the oxygen content should be less than the other two additives (Table 4). It indicates that dilution of SmI_2 with THF decreases the reduction rate. As we predicted, it does not render a linear relationship between the reaction rates and concentrations of SmI_2 . These results are consistent with what we obtained in our previous work on aldehyde and sulfoxide reductions.⁵

For 1,2-epoxydecane, the case appears more complicated. The analytical method of this compound is similar to that of 2-heptanone. However, after work-up, the unreacted reactant was converted to 1,2-dihydroxydecane which was then traced instead and satisfactory results were also obtained. Proton sources exhibit a similar catalytic effect on SmI_2 reduction of epoxide as they do on 2-heptanone (Table 5). Methanol and *t*-butanol essentially result in the same reaction rates under the same condition. However, water shows more pronounced catalytic power. Rate equations obtained for epoxide are similar to those for 2-heptanone as follows:

Table 4.^a Dependence of Pseudo-first-order Rate Constants of 2-Heptanone Reduction on Concentration of SmI_2

[SmI ₂], M	k _{ps} , sec ⁻¹
$\begin{array}{c} 9.3 \times 10^{-2} \\ 8.1 \times 10^{-2} \\ 4.5 \times 10^{-2} \end{array}$	$\begin{array}{c} 1.3 \times 10^{-5} \\ 6.7 \times 10^{-6} \\ 2.5 \times 10^{-6} \end{array}$

^a [2-heptanone]₀ = 2.0×10^{-3} M; [*t*-BuOH] = 8.3×10^{-2} M; T = 35 °C

Table 3. SmI₂ Reduction of 2-Heptanone with Different Proton Sources

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[<i>t-</i> BuOH], M	k _{ps} ^a , sec ⁻¹	[CH ₃ OH], M	k _{ps} ^a , sec ⁻¹	[H ₂ O], M	k _{ps} ^b , sec ⁻¹
1.6×10^{-1}	1.0×10^{-5}	2.0×10^{-1}	1.2×10^{-5}	4.4×10^{-1}	1.3×10^{-3}
1.2×10^{-1}	1.0×10^{-5}	1.0×10^{-1}	1.0×10^{-5}	2.2×10^{-1}	1.1×10^{-3}
1.0×10^{-2}	$9.1 \times 10^{\circ}$ 7.1×10^{-6}	5.0×10^{-2}	$6.2 \times 10^{\circ}$ 3.5 × 10 ⁻⁶	1.7×10^{-1} 1.1×10^{-1}	7.4×10^{-4} 5.4 × 10 ⁻⁴
4.2×10^{-2}	5.0×10^{-2}	2.5 ~ 10	5.5 ~ 10	1.1 ~ 10	5.4 ~ 10
2.1×10^{-2}	2.9×10^{-6}				

^a [SmI₂] = 8.1×10^{-2} M; [2-heptanone]_o = 2.0×10^{-3} M; T = 35 °C.

^b [SmI₂] = 6.2×10^{-2} M; [2-heptanone]_o = 2.0×10^{-3} M; T = 25 °C.

Table 5.ª SmI₂ Reduction of 1,2-Epoxydecane with Different Proton Sources

[<i>t</i> -BuOH], M	k_{ps}^{b} , sec ⁻¹	[CH ₃ OH], M	k_{ps}^{b} , sec ⁻¹	$[H_2O], M$	k_{ps}^{c} , sec ⁻¹
0.17	2.5×10^{-4}	0.4	3.2×10^{-4}	0.44	1.9×10^{-3}
0.084	2.0×10^{-4}	0.2	$2.7 imes 10^{-4}$	0.22	1.2×10^{-3}
0.063	1.9×10^{-4}	0.15	2.5×10^{-4}	0.11	2.5×10^{-4}
0.042	1.8×10^{-4}	0.099	2.2×10^{-4}	0.074	2.2×10^{-4}

^a [1,2-epoxydecane]_o = 1.5×10^{-3} M; T = $35 \circ$ C.

 b [SmI₂] = 0.11 M.

 $^{\circ}$ [SmI₂] = 0.062 M.

 $\begin{aligned} & Rate_{t-Butanol} = k_1`[t-BuOH][1,2-epoxydecane] \\ & Rate_{Methanol} = k_2`[CH_3OH][1,2-epoxydecane] \\ & Rate_{water} = k_3`[H_2O][1,2-epoxydecane] \end{aligned}$

where k_1 ', k_2 ', k_3 ' are approximated to be 4.8×10^{-4} , 6.0×10^{-4} , 8.6×10^{-3} , respectively.

Dependence of SmI_2 concentration on water-catalyzed reduction for this epoxide was also studied (Table 6). The rates drop with decreasing SmI_2 concentration as expected.

The results shown above suggest these proton sources can be not only just protonated to an oxygen atom of ketone or epoxide to make these molecules easier to accept electron from Sm(II), but also exhibit coordination to Sm(II) to enhance its reducing power as HMPA does. Therefore, in the case of 2-heptanone catalyzed by H_2O , the mechanism can be proposed as follows based on Kagan's mechanism⁷:

$$SmI_2 + H_2O \xleftarrow{K} C \qquad (1)$$

$$C + RCR' \longrightarrow RCR' + Sm^{-3} \qquad (2)$$

$$O \qquad OH$$

$$R\dot{C}R' + H^{+} \longrightarrow R\dot{C}R' \qquad (3)$$

$$RCR' + C \longrightarrow RCR' + Sm^{+3}$$
(4)
OH OH

$$\stackrel{\text{I}}{\text{RC}} \stackrel{\text{R'}}{\text{R'}} + \text{H}^+ \longrightarrow \stackrel{\text{I}}{\text{RC}} \stackrel{\text{I}}{\text{R'}}$$
(5)

where step (2) is the rate-determining step.

Interestingly, we did observe the color change of SmI_2 solution from blue to pink-purple immediately as H_2O was added to the SmI_2 -THF solution. However, *t*-BuOH and CH₃OH never changed the blue SmI_2 -THF solution as they were added. Water obviously coordinates with Sm(II) much better than the other two proton sources and this explains its pronounced catalytic effect. Since water is a better catalyst among the three proton sources, it should be considered useful to the samarium(II) reduction in organic syntheses. We addi-

Table 6.^a Dependence of Reaction Rates on Concentration of SmI₂

$[SmI_2], M$	k _{ps} , sec ⁻¹
0.11	5.1×10^{-3}
0.089	4.4×10^{-3}
0.062	1.9×10^{-3}
0.039	1.3×10^{-3}
$a[1,2-epoxydecane]_{a} = 1$	$.5 \times 10^{-3}$ M; [H ₂ O] = 0.44 M; T = 25 °C

tionally studied the temperature effect of this reaction for both 2-heptanone and 1,2-epoxydecane and it is obvious that higher temperature indeed effects better reduction (Table 7).

CONCLUSION

Our results indicate that in addition to HMPA, water surely can be used as another effective catalytic additive to SmI_2 reduction for certain kinds of substrates.

EXPERIMENTAL

Chemicals

Samarium iodide, decane, biphenyl, 2-heptanone, 1,2epoxydecane and t-butanol were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Hydrochloric acid and iodine were purchased from Nacalai Tesque, Inc.

Table 7. Temperature Effect on the Reduction Rates

2-heptanone ^a		1,2 epoxydecane ^b		
T, °C_	k, sec ⁻¹	Т, ℃	k, sec ⁻¹	
40	4.7×10^{-3}	45	5.18×10^{-2}	
35	3.0×10^{-3}	35	2.59×10^{-2}	
25	1.2×10^{-3}	25	1.20×10^{-2}	
		15	7.18×10^{-3}	

^a [SmI₂] = 0.11 M; [2-heptanone]_o = 1.5×10^{-3} M; [H₂O] = 0.11 M ^b [SmI₂] = 0.062 M; [1,2-epoxydecane]_o = 1.5×10^{-3} M (Kyoto, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Hexane was purchased from Tedia Company (Fairfield, OH, USA). The chemicals were used as received without further purification. Tetrahydrofuran (THF) was obtained from Labscan Ltd. (Dublin, Ireland). Methanol was obtained from Mallinckrodt Baker, Inc. (Paris, France). THF was freshly distilled and immediately transferred to a glove box before use.

General Method

Both external and internal standards were necessary for quantitative measurements of reduced substrates. A HP 6890 series GC system with a flame ionization detector (FID), an HP autosampler (Hewlett Packard Company, CA, USA), HP-5890 seriesII GC system (Hewlett Packard Company, CA, USA), HP 5971A MS (Hewlett Packard Company, CA, USA), and a split/splitless injector were used for analysis. The SISC chromatography data system (Scientific Information Service Corp., Taipei, Taiwan) and a personal computer were used for data acquisition and processing. A HP-5 column (30 m., 0.53 mm i.d., 1.5 µm film thickness, Hewlett Packard Company, CA, USA) was used for separation. Most operations were carried out in the glove box. All the reactions proceeded in a temperature controlled compartment in the glove box. In order to minimize the effect of free Sm metal in the SmI₂ solution, the solution was centrifuged prior to use and each set of experiments was conducted by using the same batch of stock solution.^{1k} The concentration of SmI₂ was determined by I₂ titration prior to reaction. In a typical experiment, 0.040 mL of water or alcohol was injected into 5.0 mL of the SmI₂ solution, subsequently, 0.040 mL of 2-heptanone or 1,2-epoxydecane in hexane was also injected and mixed thoroughly. Then, at each time interval, 0.50 mL of the reaction mixture was transferred into 0.50 mL of hexane that contained decane (for 2-heptanone) or biphenyl (for 1,2-epoxydecane) and I₂. This procedure was to ensure that the unreacted Sm(II) was quenched by I2. The I2 quenching solution was freshly prepared with an equal concentration of SmI₂. After the mixture was removed from the glove box, 0.50 mL of a 0.12 MHCl solution was added to each quenched solution and was mixed for three minutes by a Virtex mixer. The solution was set at room temperature until the organic and aqueous layers were well separated. The clear organic layer was then injected into GC for analysis. A calibration curve was constructed by plotting the ratio of the peak area of the substrate to the peak area of decane vs. the concentration of substrates. Extraction recoveries were also done. Pseudo-first-order rate constants were obtained by plotting $\log(C_t-C_{\sim})$ versus time for more than two half-lives. Here Ct and C. represent the concentrations of the substrates at time t and infinity, respectively.

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Key Words

Samarium diiodide; 2-Heptanone; 1,2-Epoxydecane.

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