Rate Study of Haloadamantane Reduction by Samarium Diiodide

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Rate constants directly measured by GC/MS-analyzed method for reduction of haloadamantanes by SmI_2 in presence of HMPA and H_2O were obtained. HMPA exhibits stronger catalytic effect than H_2O does. The result of faster reaction rate of 1-bromoadamantane than that of 2-bromoadamantane can be used to confirm the formation of alkyl radical as the rate limiting step of this reduction.

INTRODUCTION

A series of rate examinations on reduction of organic compounds including ketones, sulfoxides, alkyl halides, epoxides and esters by samarium diiodide has been accomplished previously.[1-5] GC analysis was used as the reliable method to achieve the kinetic measurement in the presence of oxygen and moisture-sensitive SmI_2. For having a better analysis of reaction products, we furthermore use GC-Mass to monitor such reactions, and the structures of the products are confirmed. Various haloadamantanes with strains were chosen as the target compounds. Besides measuring the rates of reduction for the strained alkyl halides, the reaction mechanism is clarified according to the structural effect on reduction rates.

RESULTS AND DISCUSSION

A GC-MS method was developed to determine the concentration of haloadamantanes and measure the reduction rates. In order to minimize the errors of sample preparation and GC-MS analysis, decane was used as an internal standard. The retention times of haloadamantane and decane were approximately 12.8 and 5.0 min., respectively. The linearity of GC-MS assay was established by the peak area ratio of haloadamantane/decane. Good linearity ($r^2 = 0.99$) from 0.3 to 2.0 mM was measured. The detection limit of this newly developed method was about 0.5 μM based upon three times signal-to-noise ratio. The analytical precision of this method was evaluated by replicated analysis of haloadamantane standard solutions. A total of three series of samples were analyzed over a one-week period and each sample was determined in triplicate. The intra-day and inter-day precisions showed a coefficient of variation (C.V.) ranging from 1.0% to 2.4% and 1.1% to 3.4%, respectively.

In addition, we also examined the recovery of sample preparation procedure. Known amounts (2.0, 1.0 and 0.3 mM) of 1-bromoadamantane and 1-iodoadamantane were added in a tetrahyrofuran solution and then extracted by the procedure described in the experimental section. Good recoveries ranging from 91.7% to 98.5% were determined.

For the reaction of haloadamantanes reduced by samarium diiodide, pseudo-first-order rate constants were obtained by plotting $\log(C_t\text{-}C_\infty)$ versus time for more than two half-lives. Here C_t and C_∞ represent the concentration of haloadamantanes at time t and infinity, respectively (Fig. 1). The pseudo-first-order rate constants were also tested by using different initial concentrations of the reactant (Table 1). Both

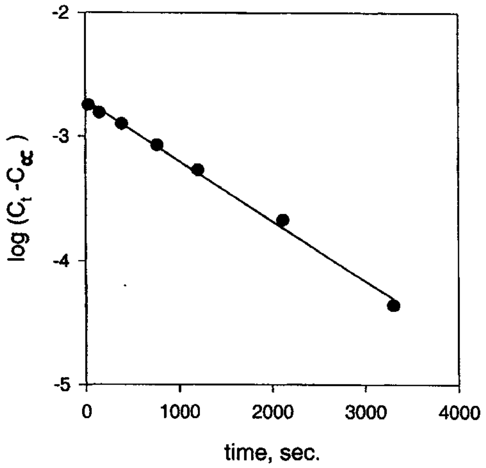

Fig. 1. Pseudo first-order rate plot of SmI_2 reduction of 1-iodoadamantane; $[SmI_2] = 7.2 \times 10^{-2}$ M, $[H_2O] = 4.4 \times 10^{-1}$ M, $[\text{1-iodoadamantane}]_o = 2.0 \times 10^{-3}$ M, T = 25 ℃.

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Table 1[a]. Dependence of Pseudo-first-order Rate constants on Initial Concentration of Haloadamantanes

[1-Bromoadamantane]$_0$, M	$k_{ps}{}^a$, sec^{-1}	[1-Iodoadamantane]$_0$, M	$k_{ps}{}^b$, sec^{-1}
4.0×10^{-3}	1.2×10^{-3}	4.0×10^{-3}	3.3×10^{-3}
2.0×10^{-3}	1.3×10^{-3}	2.0×10^{-3}	3.2×10^{-3}
1.0×10^{-3}	1.3×10^{-3}	1.0×10^{-3}	3.3×10^{-3}

[a] $[SmI_2] = 6.7 \times 10^{-2}$ M; [HMPA] = 9.2×10^{-2} M; T = 25 °C.

[b] $[SmI_2] = 6.2 \times 10^{-2}$ M; $[H_2O] = 8.9 \times 10^{-2}$ M; T = 25 °C.

k_{ps} represents pseudo-first-order rate constant.

cases of bromoadamantane and iodoadamantane reductions exhibit the same k_{ps} with different initial concentrations of haloadamantane, i.e., these reductions fit perfectly pseudo-first-order in these substrates. Here catalysts such as water or hexamethylphosphoramide were necessary for effecting the reduction. In order to minimize the effect of Sm metal powder on reduction rate, samarium diiodide solution was centrifuged prior to reaction. The product was traced and characterized as adamantane with an authentic sample by GC-MS chromatography.

Both water and hexamethylphosphoramide (HMPA) catalyze this reduction. Yet as expected, HMPA is more efficient than water. However, in the presence of HMPA, the pseudo-first-order linear plot can be obtained only for fast reactions (within 10 minutes) while the curvature appeared for slow reactions. This can be accounted for by the slow reaction between SmI_2 and HMPA.[6] Under our reaction condition, we solved this problem simply by taking the initial rates for slow reactions since at the beginning of the reaction, the linearity for the first-order relationship still can be obtained. Fig. 2 shows the catalytic effect of H_2O on reduction of 1-iodoadamantane by SmI_2. Good linearity was achieved to give a relationship as follows:

$$k_{ps} = k_1[H_2O]$$

Since

$$\text{Rate} = k_{ps}[\text{1-iodoadamantane}]$$

therefore,

$$\text{Rate} = k_1[H_2O][\text{1-iodoadamantane}]$$

The slope of the straight line obtained in Fig. 2 can be used to calculate k_1 as 6.3×10^{-3} sec^{-1}M^{-1} that is dependent on $[SmI_2]$ and temperature. This result is consistent with Hasegawa and Curran's work[7] which presented evidence that water serves not only as a proton source, but can also accelerate certain classes of samarium reductions. We, however, are able to obtain absolute rates instead of relative rates which were measured from reactant to product ratios. Fig. 3 shows the catalytic effect of HMPA on reduction of 1-bromoadamantane by SmI_2. The induction period of this figure can be explained by the slow reaction between SmI_2 and HMPA, i.e., a small amount of HMPA is consumed by SmI_2. The following relationship can be derived as

$$k_{ps} = k_2[\text{HMPA}]$$

for the linear part of this graph.

Since

$$\text{Rate} = k_{ps}[\text{1-bromoadamantane}]$$

therefore,

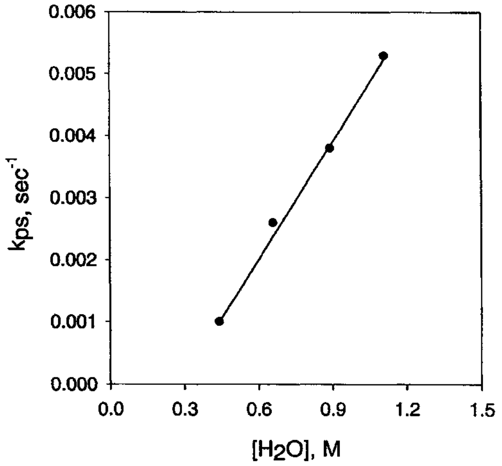


Fig. 2. Dependence of water concentration on pseudo first-order rate constant $[SmI_2] = 7.2 \times 10^{-2}$ M, [1-iodoadamantane]$_0$ = 2.0×10^{-3} M, T = 25 °C.

Table 2[a]. SmI_2 Reduction of 1-Haloadamantane

1-Haloadamantane	k_{ps}[b](H_2O catalyzed)	k_{ps}[c](HMPA catalyzed)
RCl	--[d]	5.1×10^{-6}
RBr	7.5×10^{-5}	1.3×10^{-3}
RI	5.3×10^{-3}	8.0×10^{-2}

[a] $[SmI_2] = 7.3 \times 10^{-2}$ M; $[RX]_0 = 2.0 \times 10^{-3}$ M; T = 25 °C; k_{ps} represents pseudo-first-order rate constant.
[b] $[H_2O] = 1.1$ M.
[c] $[HMPA] = 6.9 \times 10^{-2}$ M.
[d] too slow to measure.

$$\text{Rate} = k_2[\text{HMPA}][\text{1-bromoadamantane}]$$

for the linear part of this graph, and the slope obtained can be used to calculate k_2 which is dependent on $[SmI_2]$ and temperature. Under our reaction condition, k_2 is approximated to be 5.3×10^{-3} $sec^{-1}M^{-1}$.

Either H_2O or HMPA catalyzed reduction exhibits the reaction rates in the increasing order of 1-chloroadaamantane < 1-bromoadamantane < 1-iodoadamantane (Table 2). This reasonable result is fully consistent with that of unstrained alkyl halides.[3]

The rates of 1-bromoadamantane and 2-bromoadamantane were compared carefully in order to examine the mechanism. Table 3 indicates 1-bromoadamantane is reduced faster than 2-bromoadamantane, i.e., tertiary bromoadamantane reacts with samarium diiodide faster than secondary bromoadamantane does. This piece of information confirms that the rate determining step involves the formation of adamantane radical instead of an adamantane anion.

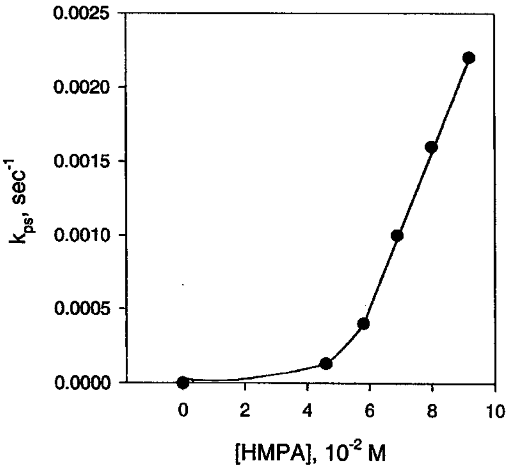


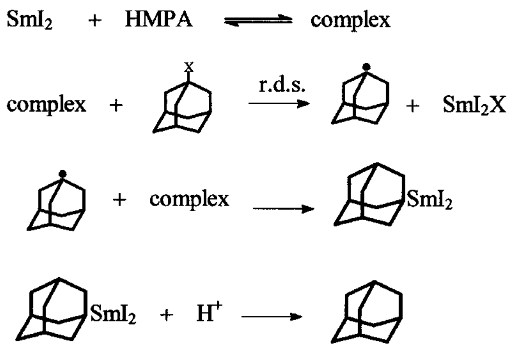
Fig. 3. Dependence of HMPA concentration on pseudo first-order rate constant $[SmI_2] = 7.0 \times 10^{-2}$ M, $[\text{1-bromoadamantane}]_0 = 2.0 \times 10^{-3}$ M, T = 25 °C.

Table 3[a]. Structural Effect of Bromoadamantane on Reduction Rates

Bromoadmantane	k_{ps}, sec^{-1}
1-bromoadamantane(tert-RBr)	5.4×10^{-4}
2-bromoadamantane(sec-RBr)	3.1×10^{-4}

[a] $[SmI_2] = 6.2 \times 10^{-2}$ M; $[RX]_0 = 2.0 \times 10^{-3}$ M; $[HMPA] = 6.9 \times 10^{-2}$ M; T = 25 °C; k_{ps} represents pseudo-first-order rate constant.

The mechanism thus can be proposed as follows:



Finally, temperature effect was examined (Table 4) which shows a similar result with that of our previous work,[4,5] i.e., this reduction is favored at higher temperatures.

CONCLUSION

In summary, by GC/MS analyzing method, we have obtained the pseudo-first-order rate constants of the reduction of strained molecules of haloadamantanes that are less reactive toward SmI_2 than unstrained alkyl halides.[3] Radical formation is confirmed as the rate determining step.

Table 4[a]. Temperature Effect on Reaction Rate

T, °C	k_{ps}[b], sec^{-1}
40	1.3×10^{-3}
34	9.3×10^{-4}
24	5.0×10^{-4}
16	2.7×10^{-4}

[a] $[SmI_2] = 0.11$ M; $[\text{1-bromoadamantane}]_0 = 2.0 \times 10^{-3}$ M; $[HMPA] = 6.9 \times 10^{-2}$ M.
[b] k_{ps} represents pseudo-first-order rate constant.

EXPERIMENTAL

Chemicals

Samarium iodide, decane, 1-chloroadamantane, 1-bromoadamantane, 1-iodoadamantane, 2-bromoadamantane and hexamethyl phosphoramide (HMPA) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Hydrochloric acid and iodine were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Hexane was purchased from Tedia Company (Fairfield, OH, USA). Tetrahydrofuran (THF) was purchased from Labscan Ltd. (Dublin, Ireland). The chemicals were used as received without further purification. 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 haloadamantanes. A HP 6890 series GC system with a flame ionization detector (FID), a 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 SmI$_2$ solution, each set of experiments was conducted by using the same batch of stock solution.[11k] The concentration of SmI$_2$ was determined by I$_2$ titration prior to reaction. In a typical experiment, 0.030 mL of the haloadamantanes in hexane or THF was injected into 5.0 mL of the SmI$_2$ solution and mixed thoroughly. Subsequently, at each time interval, 0.50 mL of the reaction mixture was transferred into 0.50 mL of hexane that contained decane and I$_2$. This procedure was to ensure that the unreacted Sm(II) was quenched by I$_2$. The I$_2$ quenching solution was freshly prepared with an equal concentration of SmI$_2$. After the mixture was removed from the glove box, 0.50 mL of a 0.12 M HCl solution was added to each quenched solution and was mixed 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$_\infty$) versus time for more than two half-lives. Here C$_t$ and C$_\infty$ represent the concentration of haloadamantanes at time t and infinity, respectively.

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Key Words

Samarium diiodide; Haloadamantane.

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