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PHOTOREDUCTION OF CARBONYLS WITH HYDROGEN SELENIDE.¹⁾ AN ESTIMATION OF THE HIGH HYDROGEN DONATING ABILITY OF HYDROGEN SELENIDE BY KINETIC STUDY AND CHEMICAL TRAPPING

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The rate constant for the photoreduction of acetophenone with hydrogen selenide in tetrahydrofuran was obtained as 4.7X10⁸ $M^{-1}s^{-1}$. It was also found that hydrogen selenide was able to trap short-lived excited carbonyls, and acyl or alkyl radicals generated in Norrish type I reaction.

In our previous paper²⁾ we have described a new photoreduction of carbonyls to corresponding carbinols without producing pinacol derivatives in the presence of hydrogen selenide. This result has prompted us to measure the rate constants of this photoreduction.

First, the rate constant k_r for the reduction of acetophenone, reaction (1), was obtained by a Stern-Volmer treatment.

$$\begin{array}{c} O \\ \parallel \\ PhCCH_3 + H_2Se \end{array} \xrightarrow{313 \text{ nm}} \begin{array}{c} OH \\ \parallel \\ THF \end{array} \xrightarrow{PhCHCH_3} + Se$$
 (1)

A relevant reaction mechanism for the photoreduction of acetophenone with hydrogen selenide is shown in Scheme 1, where K represents acetophenone, the superscripts 1 and 3 correspond to excited singlet and triplet states, and Q represents biphenyl as a triplet quencher. The rate constant for the deactivation of ³K with hydrogen selenide by some interactions is represented by $k_q^{H_2}^{Se}$. Thus the quantum yield Φ of α -phenethyl alcohol formation is given as

$$\Phi = \frac{k_{r}[H_{2}Se]}{k_{d} + k_{q}[Q] + (k_{q}^{H_{2}Se} + k_{r})[H_{2}Se]}$$
(eq.1)

Stern-Volmer plots fall on straight lines as shown in Figures 1 and 2. The quenching rate constant k_q is estimated to be 9.1 X 10⁹ M⁻¹s⁻¹,³) and k_d is much smaller⁴ than ($k_q^{H_2Se} + k_r$)[H₂Se], therefore k_d is neglected. With these assumptions and data from Figures 1 and 2, where [H₂Se] = 0.21 M, we obtain

$$k_r = 4.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$

 $k_q^{\text{H}2^{\text{Se}}} = 6.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$

These values lead to $\Phi = 0.41$ from eq. 1, which is in good agreement with the quantum yield (0.40) estimated from the value of the intercept in Figure 1. The rate constant obtained is much larger than the reported values⁵⁾ which are in the order of $10^{6} \text{ M}^{-1} \text{s}^{-1}$ for the photoreduction of acetophenone with 2-propanol. This result is important supporting evidence for the high hydrogen donating ability of hydrogen selenide which may be due to the weak hydrogen-selenium bond.⁶⁾



- $K + hv \frac{100\%}{5} K$
 - ¹_K <u>~100%</u> ³_K
 - ³к ^kd **ж** к
- ${}^{3}K + Q \xrightarrow{k_{q}}$ quenching
- ${}^{3}K$ + ${}^{H_{2}Se} \xrightarrow{q}$ quenching
- ${}^{3}K$ + ${}^{H}_{2}Se \xrightarrow{k_{r}}$ carbinol



Figure 1. Stern-Volmer plot for the reduction of acetophenone(0.1 M) with hydrogen selenide (0.21 M) at 313 nm employing biphenyl as a triplet quencher,Q, at 20°C in THF.



Figure 2. Stern-Volmer plot. Conditions are the same as in Figure 1.

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Secondly, the photoreduction of dibenzyl ketone (0.041 M) with hydrogen selenide (0.21 M) was investigated, since the photolysis of the ketone in the absence of hydrogen selenide is known to undergo rapid Norrish type I reaction. The products and their amounts (µmol) are shown in the reaction (2).

$$\begin{array}{cccc} & & & & & & & \\ & & & & & & \\ PhCH_2CCH_2Ph & & & & & \\ & & & & & & \\ 100 \ \mu mol \end{array} \xrightarrow{H_2Se} & & & OH & & & OH \\ & & & & & & \\ PhCH_2CHH_2Ph & & & PhCH_2CH + PhCH_2CH_2 + PhCH_3 & (2) \\ & & & & & \\ 100 \ \mu mol \end{array}$$

The formation of dibenzylcarbinol suggests that the reduction of photoexcited dibenzyl ketone⁷⁾ in singlet and/or triplet states with hydrogen selenide competes the α -cleavage. The rate constant for the photoreduction of dibenzyl ketone with hydrogen selenide might be estimated at least in the order of 1.6 X 10⁸ M⁻¹s⁻¹. β -Phenethyl alcohol is considered to be formed by the reduction of phenylacetaldehyde produced by the trapping of the acyl radical (PhCH₂C·) generated in Norrish type I reaction. 1,2-Diphenylethane was not detected and toluene was formed. These results suggest that benzyl radical is trapped much faster than its coupling. The photoreduction of phenylacetaldehyde was successfully carried out under the similar reaction conditions, reaction (3).

$$\begin{array}{cccc} & & & & & & & \\ & & & & & & \\ PhCH_2CH & & & & & \\ & & & & & \\ & & & & \\ 100 \ \mu mol & & & & \\ \end{array} \begin{array}{c} & & & & \\ HF & & & \\ & & & \\ & & & \\ \hline \end{array} \begin{array}{c} & & & \\ PhCH_2CH_2 & + & PhCH_3 & & (3) \\ & & & \\ & & & \\ 100 \ \mu mol & & & \\ \end{array} \begin{array}{c} & & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \hline \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \end{array}$$

In this reaction, $10 \ \mu$ mol of phenylacetaldehyde was remained unreacted. Material balances in these reactions (2) and (3) were excellent.

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References and Notes

- To be regarded as Part I of photoreduction with hydrogen selenide.
 For Part I see ref. 2.
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