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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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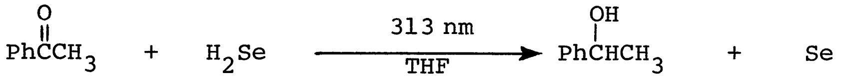
The rate constant for the photoreduction of acetophenone with hydrogen selenide in tetrahydrofuran was obtained as 4.7×10^{8} $M^{-1}s^{-1}$. It was also found that hydrogen selenide was able to trap short-lived excited carbonyls, and acyl or alkyl radicals generated in Norrish type I reaction.

In our previous paper[2) 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.



$$PhC(=O)CH_3 + H_2Se \xrightarrow[THF]{313\text{ nm}} PhCH(OH)CH_3 + Se \qquad (1)$$

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 $k_q^{H_2Se}$. Thus the quantum yield Φ of α-phenethyl alcohol formation is given as

$$\Phi = \frac{k_r[H_2Se]}{k_d + k_q[Q] + (k_q^{H_2Se} + k_r)[H_2Se]} \qquad (\text{eq. } 1)$$

Stern-Volmer plots fall on straight lines as shown in Figures 1 and 2. The quenching rate constant k_q is estimated to be $9.1 \times 10^9\ M^{-1}s^{-1}$,3) and k_d is much smaller4) than ($k_q^{H_2Se}$ + k_r)$[H_2Se]$, therefore k_d is neglected. With these assumptions and data from Figures 1 and 2, where $[H_2Se] = 0.21$ M, we obtain

$$k_r = 4.7 \times 10^8\ M^{-1}s^{-1}$$
$$k_q^{H_2Se} = 6.7 \times 10^8\ M^{-1}s^{-1}$$

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 $10^6\ M^{-1}s^{-1}$ 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)

Scheme 1.

$$K + h\nu \xrightarrow{\sim 100\%} {}^1K$$
$${}^1K \xrightarrow{\sim 100\%} {}^3K$$
$${}^3K \xrightarrow{k_d} K$$
$${}^3K + Q \xrightarrow{k_q} \text{quenching}$$
$${}^3K + H_2Se \xrightarrow{k_q^{H_2Se}} \text{quenching}$$
$${}^3K + H_2Se \xrightarrow{k_r} \text{carbinol}$$

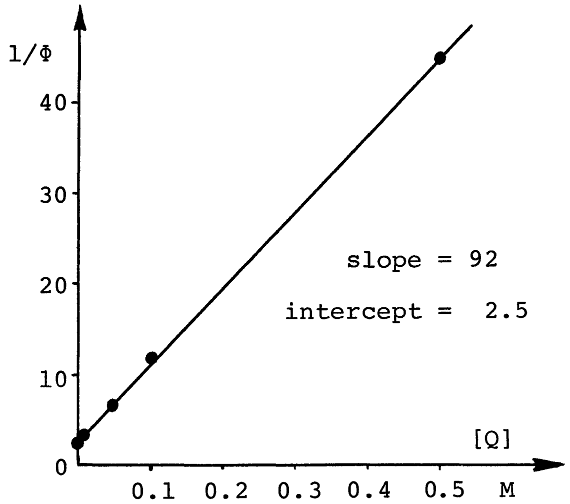


Figure 1. Stern-Volmer plot for the reduction of acetophenone(0.1 M) with hydrogen selenide (0.21 M) at 313 nm employing biphenyl as a triplet quencher,Q, at 20°C in THF.

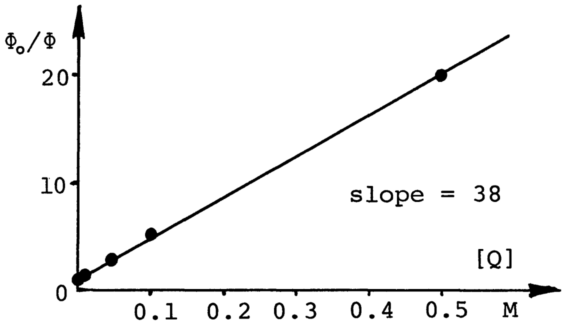
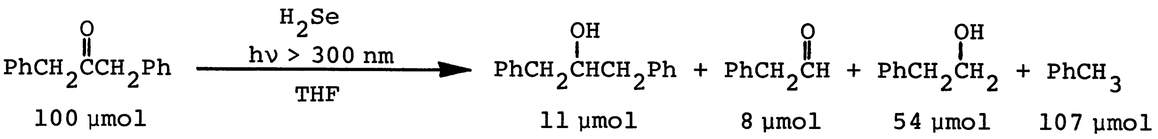


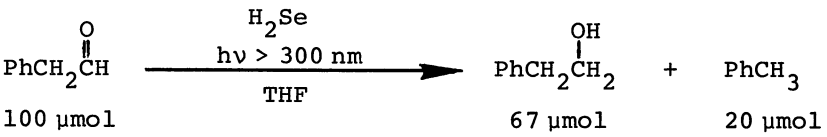
Figure 2. Stern-Volmer plot. Conditions are the same as in Figure 1.

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).



$$\underset{100\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph}} \xrightarrow[\mathrm{THF}]{\substack{\mathrm{H_2Se} \\ h\nu > 300\ \mathrm{nm}}} \underset{11\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{OH}{\overset{|}{C}}HCH_2Ph}} + \underset{8\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}H}} + \underset{54\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{OH}{\overset{|}{C}}H_2}} + \underset{107\ \mu\mathrm{mol}}{\mathrm{PhCH_3}} \qquad (\ 2\ )$$

The formation of dibenzylcarbinol suggests that the reduction of photoexcited dibenzyl ketone[7)] 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 $1.6 \times 10^8\ \mathrm{M^{-1}s^{-1}}$. β-Phenethyl alcohol is considered to be formed by the reduction of phenylacetaldehyde produced by the trapping of the acyl radical ($\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}\cdot}$) 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).



$$\underset{100\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{O}{\overset{\|}{C}}H}} \xrightarrow[\mathrm{THF}]{\substack{\mathrm{H_2Se} \\ h\nu > 300\ \mathrm{nm}}} \underset{67\ \mu\mathrm{mol}}{\mathrm{PhCH_2\overset{OH}{\overset{|}{C}}H_2}} + \underset{20\ \mu\mathrm{mol}}{\mathrm{PhCH_3}} \qquad (\ 3\ )$$

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

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References and Notes

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

2) N. Kambe, K. Kondo, S. Murai, and N. Sonoda, Angew. Chem. Int. Ed. Engl., in press.

3) The quenching rate constant of the triplet excited state of acetophenone with naphthalene in benzene was reported as $7.7 \times 10^9\ M^{-1}s^{-1}$; W. D. K. Clark, A. D. Litt, and C. Steel, J. Am. Chem. Soc., 91, 5413(1969). If the rate constant of quenching is assumed to be solely dependent on the viscosity of the solvent, k_q in THF is calculated as $9.1 \times 10^9\ M^{-1}s^{-1}$.

4) Reported lifetimes of the triplet excited state of acetophenone in benzene and in 2-propanol were 3.5 and 0.41 μsec respectively; S. L. Murov, " Handbook of Photochemistry," Marcel Dekker, New York, 1973, p. 3.

5) H. Lutz, M. -C. Duval, E. Bréhéret, and L. Lindqvist, J. Phys. Chem., 76, 821(1972).

6) The bond energy of hydrogen-selenium bond was described as 73 kcal/mol; S. R. Gunn, J. Phys. Chem., 68, 949(1964); M. Schmidt, W. Siebert, and K. W. Bagnall," The Chemistry of Sulphur, Selenium, Tellurium, and Polonium," Pergamon Press, New York, 1973, p. 954. C. M. Previtali, J. C. Scaiano, J. Chem. Soc., Perkin Trans. II, 1672(1972).

7) Lifetimes of singlet and triplet states of dibenzyl ketone in benzene were estimated as 3.6 and 0.1 nsec respectively; P. S. Engel, J. Am. Chem. Soc., 92, 6074(1970).

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