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MECHANISTIC ASPECTS OF FLUORIDE ION-CATALYZED REDUCTION OF CARBONYL COMPOUNDS WITH HYDROSILANES

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Fluoride ion catalyzed reduction of aldehydes and ketones with hydrosilane in HMPA is found to involve a hexavalent silicate $[HSiR_3F(HMPA)]^-$ *as the active hydride species, and no evidence is obtained for interaction of the carbonyl oxygen with the silicon.*

Fluoride ion-catalyzed hydrosilylation of carbonyl compounds (eq 1) is of current interest from both synthetic[1,2] and mechanistic[3] viewpoints. This reduction is shown to proceed mainly via a hydride transfer,[3] and a pentavalent fluorosilicate $[HSiR_3F]^-$ (**1**) is assumed[2a,3] as the active hydride species. Since **1** has still a vacant coordination site, a four-centered transition state may be involved, wherein the carbonyl oxygen coordinates to the silicon.[4] Elucidation of the mechanistic feature of this reduction is significant in association with those of the fluoride ion-catalyzed reactions of various organosilicon compounds.[5]

This paper describes following new mechanistic aspects of this reaction: i) the active species is a solvent-coordinated hexavalent silicate (**2**) formed by eqs 2 and 3; ii) hence, the $O\rightarrow Si$ coordination in the transition state is not involved; and iii) an alternative activation of the carbonyl group by R_3SiF is also ruled out.

$$R^1COR^2 + HSiR_3 \xrightarrow{F^-} R^1CH(OSiR_3)R^2 \qquad (1)$$

$$\left\{\begin{array}{ll} H\text{-}SiR_3 + F^- \rightleftharpoons \underset{\textbf{1}}{[H\text{-}SiR_3F]^-} & (2) \\ \textbf{1} + HMPA \rightleftharpoons \underset{\textbf{2}}{[H\text{-}SiR_3F(HMPA)]^-} & (3) \\ R^1COR^2 + \textbf{2} \longrightarrow R^1CH(O^-)R^2 + FSiR_3(HMPA) & (4) \end{array}\right.$$

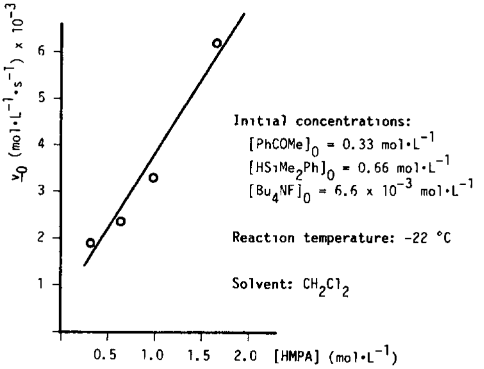
The rate determining step of this reduction was shown to be the hydride transfer step[6] as judged by a significant isotope effect observed in the reduction of acetophenone with $DSiMe_2Ph$:[7] the ratio of the reaction rate $\underline{v}_H/\underline{v}_D = 1.50$ (eq 5). The reaction was also shown to

$$PhCOMe + \underset{(D)}{HSiMe_2Ph} \xrightarrow[2.\ H_3O^+]{1.\ F^-} \underset{(D)}{PhCH(OH)Me} \qquad \underline{v}_H/\underline{v}_D = 1.50 \qquad (5)$$

be markedly accelerated by the employment of aprotic polar solvents like hexamethylphosphoric triamide (HMPA).[8] In paticular, the initial reaction rate $\underline{v}_0$ for the reduction of acetophenone with dimethylphenylsilane was proved to be proportional to the concentration of HMPA (Fig. 1).[9] These kinetic data strongly suggest the equilibrium of eqs 2 and 3 does exist, by which a hexavalent silicate (**2**) is formed. Being fully coordinated, this delivers hydride without coordination at the carbonyl oxygen (eq 4). The naked alkoxide thus formed is immediately trapped by the solvent-coordinated fluorosilane.

Another possibility for the carbonyl activation arises which involves coordination of R_3SiF to $>C=O$, since R_3SiX is expected to be a weak Lewis acid.[10] When c-$C_6H_{11}CHO$ and $HSiMe_2$(p-Tol) were treated with a fluoride ion catalyst in the presence of an equimolar amount of $FSiMe_2Ph$, the products at the early stage of the reduction consisted mainly of the dimethyl(p-tolyl)silyl ether **5**, which later underwent extensive silyl exchange by F^- to give a 1 : 1 mixture of **5** and **6** (eq 6).[11] These results clearly exclude a fluorosilane-participated mechanism and indicate that H and R_3Si originate from a single molecule $HSiR_3$.[12]

Fig. 1. v_0 v.s. [HMPA]



$$\underline{c}\text{-}C_6H_{11}CHO + HSiMe_2(\underline{p}\text{-Tol}) \xrightarrow{a} \underline{c}\text{-}C_6H_{11}CH_2OSiMe_2Ar \quad (\mathbf{5}\text{: Ar} = \underline{p}\text{-Tol; } \mathbf{6}\text{: Ar = Ph}) \qquad (6)$$

a: $FSiMe_2Ph$ (1 mol); $(Et_2N)_3S^+Me_3SiF_2^-$ (5 mol%); HMPA; 0 °C, 2 h - rt, 10 h

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12. This work was supported in part by a Grant-in-aid for Special Research on Organic Chemical Resources (61111001) from the Ministy of Education, Science and Culture, Japan.

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