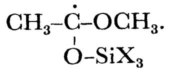
932 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 932—934 (1974) [Vol. 47, No. 4

The Reduction of Methyl Acetate with Several Hydrosilanes under γ Irradiation

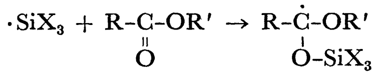
Ren Nakao, Tsugio Fukumoto, and Jitsuo Tsurugi
Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka 593

(Received July 13, 1973)

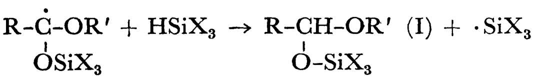
The reduction of methyl acetate with chlorinated hydrosilanes, $HSiCl_{3-n}R_n$ ($R=CH_3$ or OCH_3, $n=0$—2), and triethylsilane under γ irradiation has been studied. The hydrosilanes other than triethylsilane reduce the ester to ethyl methyl ether. The reaction rate is proportional to the hydrosilane concentration and is independent of the methyl acetate concentration. The results indicate that the rate-determining step in the reduction reaction is the hydrogen abstraction from the hydrosilanes. The reactivities of the chlorinated hydrosilanes in the reaction increase with the progressive chlorine substitution on the silicon atom and may be due to the susceptibility of each H-Si bond toward free radicals, $CH_3\text{-}\underset{\text{O-SiX}_3}{\dot{C}}\text{-}OCH_3$.



Previously, we reported that the aliphatic carboxylates can be reduced to dialkyl ethers with trichlorosilane under γ irradiation.[1] Kinetic work[2] on this reduction and the reduction of acetals[3] with trichlorosilane have indicated that the mechanism for the reduction of the ester with trichlorosilane consists of three sequences. The first is the radical-chain addition of trichlorosilane to a carbonyl group of a carboxylate (Eqs. (1) and (2)). The second is the ionic chlorination of the adduct (I) by chlorosilanes, giving an α-chloro ether (II) (Eq. (3)). The third is the reduction of α-chloro ether to an ether with trichlorosilane (Eqs. (4) and (5)).



$$\cdot SiX_3 + R\text{-}\underset{\text{O}}{\overset{\|}{C}}\text{-}OR' \rightarrow R\text{-}\underset{\text{O-SiX}_3}{\dot{C}}\text{-}OR' \qquad (1)$$



$$R\text{-}\underset{\text{OSiX}_3}{\dot{C}}\text{-}OR' + HSiX_3 \rightarrow R\text{-}\underset{\text{O-SiX}_3}{CH}\text{-}OR'\ (I) + \cdot SiX_3 \qquad (2)$$

$$(I) + Cl\text{-}Si\lessdot \rightarrow R\text{-}CHCl\text{-}OR'\ (II) + X_3SiOSi\lessdot \qquad (3)$$

$$(II) + \cdot SiX_3 \rightarrow R\text{-}\dot{C}H\text{-}OR' + ClSiX_3 \qquad (4)$$

$$R\text{-}\dot{C}H\text{-}OR' + HSiX_3 \rightarrow R\text{-}CH_2\text{-}OR' + \cdot SiX_3 \qquad (5)$$

It seems interesting to examine whether chlorinated hydrosilanes containing the general formula $HSiCl_{3-n}R_n$ ($R=CH_3$ or OCH_3, $n=0$—2) can be used in the reduction of the ester, and, if so, which is the most efficient reagent. With these points in view, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, methoxydichlorosilane, dimethoxychlorosilane, and triethylsilane were allowed to react with methyl acetate and acetaldehyde dimethyl acetal under γ irradiation.[4]

Results and Discussion

All the reactions were carried out in tetrachlorosilane as a solvent. Our previous paper[3] reported that all chlorinated silanes including tetrachlorosilane can chlorinate an acetal-type intermediate (I) to an α-chloro ether (II) in Eq. (3), and that the chlorination is instantaneous. In the present experiments, tetrachlorosilane as a solvent behaves as the chlorinating agent[5] in Eq. (3), and the chlorinated hydrosilanes ($HSiCl_{3-n}R_n$) used may be regarded as participating only in the first sequence (Eqs. (1) and (2)) and the third sequence (Eqs. (4) and (5)).

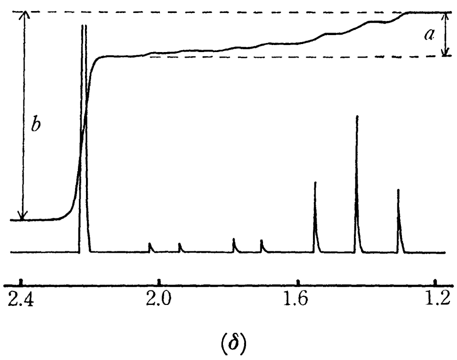


Fig. 1. NMR spectrum and integration curve of an irradiated mixture of methyl acetate and trichlorosilane (see the footnote (a) in Table 1), where singlet at δ 2.22 was attributable to $CH_3C(O)$- of methyl acetate, and two doublets at δ 1.74 and 1.98, and triplet at δ 1.43 were assigned to the corresponding methyl protons of the adduct, α-chloroethyl methyl ether, and ethyl methyl ether, respectively. Dose rate; 1.7 M rad/h and dose; 0.9 M rad.

A typical example of the NMR spectrum of a γ-irradiated mixture of methyl acetate and trichlorosilane in tetrachlorosilane is shown in Fig. 1. Small amounts of the adduct ((I), in which $R=R'=CH_3$ and $X=Cl$) and α-chloroethyl methyl ether were detected, together with the unchanged ester and the ethyl methyl ether produced.

In order to shed light on the mechanism, it seems necessary to determine the rates of the first sequence (adduct formation) and the third sequence (the reduction of α-chloro ether) separately. Because of the (ester→I→II→ether) sequence and the equimolar relationship[2] between species, the rate of the adduct formation at any given reactant concentration can be obtained by determining the total sum of the adduct, the α-chloro ether, and the ether in the reaction system. When a mixture of a hydrosilane and methyl acetate (3 : 1 molar ratio) in tetrachlorosilane was irradiated for various time periods, a plot of the total sum against the irradiation time was found to be a straight line up to *ca.* a 30% conversion of methyl acetate. The rates of the adduct formation, which were calculated from

Table 1. Rates of the reactions with several hydrosilanes

Hydrosilane	Rate of reduction[a] (mol/l·h), (A)	Rate of reduction[b] (mol/l·h), (B)	R_{add}/R_{red}[c] (2A/3B)
$HSiCl_3$	0.76	0.77	0.66
$HSiCl_2Me$	0.15	0.13	0.79
$HSiCl_2OMe$	0.09	0.14	0.44
$HSiClMe_2$	0.05	0.08	0.41
$HSiCl(OMe)_2$	0.03	0.05	0.39

Dose rate; 1.7 M rad/h. a) CH_3COOCH_3; 0.7 mmol; hydrosilane; 2.1 mmol, $SiCl_4$; 1 ml. b) $CH_3CH(OCH_3)_2$; 0.7 mmol, hydrosilane; 1.4 mmol, $SiCl_4$; 1 ml. c) This value was corrected by a factor of 2/3, since the addition and reduction reactions were carried out with 3 : 1 aad 2 : 1 molar excess of each hydrosilane, respectively, and the rates of both reactions were proportional to hydrosilane concentration as described in the text. Detailed calculations on the concentrations of each hydrosilane in both the addition and reduction reactions show that the factor 2/3 is approximately correct to obtain the ratio R_{add}/R_{red} at the same concentration.

the respective slopes of the straight lines for five hydrosilanes, are shown in Table 1.

As to the third sequence, we can utilize the following reaction. Our previous paper[3] reported that the simple mixing of acetaldehyde dimethyl acetal and tetrachlorosilane gave α-chloroethyl methyl ether.

$$CH_3CH(OCH_3)_2 + Cl_4Si \rightarrow CH_3CHClOCH_3 + Cl_3SiOCH_3$$

Therefore, acetaldehyde dimethyl acetal in tetrachlorosilane was allowed to react with hydrosilanes (1 : 2 molar ratio) under γ irradiation. The rates of the reduction of the α-chloro ether at given reactant concentrations can be obtained by determining the amount of ethyl methyl ether produced, these rates are shown in Table 1 (the time plot is a straight line in this case also). In both reactions (the addition to the carboxylate and the reduction of the α-chloro ether), the reactivities of the hydrosilanes increase with progressive chlorine substitution on the silicon atom, as Table 1 shows.

R_{add}/R_{red}, the ratio of the rate of the addition to that of the reduction at the same hydrosilane concentration for the individual hydrosilane, is given in the last column of Table 1. All of the ratios are smaller than unity. This result clearly indicates that the adduct formation is rate-determining. This is consistent with the fact that little α-chloroethyl methyl ether was detected in the reaction mixture when hydrosilanes other than methyldichlorosilane were used. When methyldichlorosilane was used, however, the α-chloro ether was detected by NMR. This result coincides with the R_{add}/R_{red} ratio for methyldichlorosilane, which is 0.79—the largest in the series.

The dependence of both rates on the reactant concentrations was investigated by using methoxydichlorosilane as a representative. The results for the addition to methyl acetate and for the reduction of α-chloroethyl methyl ether are shown in Figs. 2 and 3 respectively, where the (a) lines give a run with a constant methoxydichlorosilane concentration and with various concentrations of methyl acetate or acetaldehyde dimethyl acetal, while the (b) lines show one with a constant concentration of the ester or the acetal and with various concentrations of the hydrosilane. The two slopes calculated from the (a) and (b) lines in Fig. 2 were 0.05 and 0.97, while those obtained from Fig. 3 were zero and 0.93, respectively. Thus, both the addition and reduction reaction rates were proportional to the methoxydichlorosilane concentration and were independent of the carboxylate or acetal concentration. The same dependence had been observed in the addition reaction of trichlorosilane[2] to the ester (the first sequence in the reduction of the ester). The results

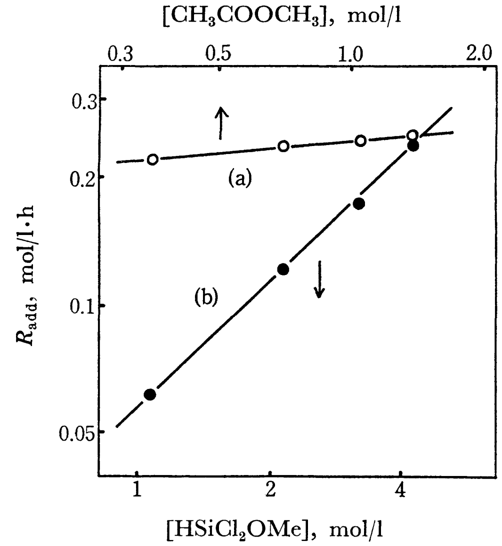


Fig. 2. Variation in the rate of the adduct formation with reactant concentrations under a given dose rate of 1.7 M rad/h. (a); $[HSiCl_2OMe]=4$ mol/l, (b); $[CH_3COOCH_3]=0.7$ mol/l.

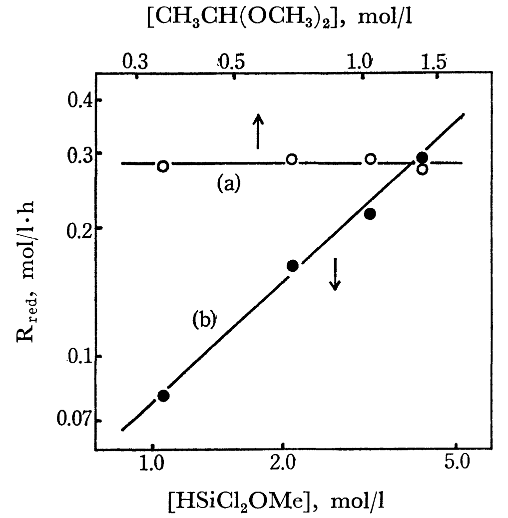


Fig. 3. Variation in the rate of the reduction of α-chloroethyl methyl ether with reactant concentrations under a given dose rate of 1.7 M rad/h. (a); $[HSiCl_2OMe]=4$ mol/l, (b); $[CH_3CH(OCH_3)_2]=0.7$ mol/l.

presented above suggest that the rate-determining step of the addition sequence is Eq. (2), while that of the reduction sequence of the α-chloro ether is Eq. (5). The results mean that the hydrogen abstraction steps are rate-determining in both sequences.

When γ irradiation is carried out under the same conditions, the rate of the radical formation may be regarded as identical in all the reactions using any hydrosilane. Therefore, we concluded that the rates in Table 1 correspond to the reactivities of each Si–H bond toward either $CH_3\text{-}\underset{O\text{-}SiX_3}{\dot{C}}\text{-}OCH_3$ or $CH_3\text{-}\dot{C}H\text{-}OCH_3$. The reactivity increases with the progressive introduction of chlorine, which is an electron-withdrawing atom, on the silicon atom. The reactivities of Me_3SiH, $MeCl_2SiH$, and Cl_3SiH for hydrogen abstraction by methyl radicals have been reported⁶⁾ to increase consistently with an increase in the amount of chlorine on the silicon atom. Nagai and Sakurai⁷⁾ described that an electron-withdrawing group on a silicon atom decreases the contribution of $\geqslant Si^+H^-$ in the resonance formula: $\geqslant Si\text{-}H \leftrightarrow \geqslant Si^+H^-$, thus causing the bond strength of Si–H to become weak. In this connection, the reactivities of hydrosilanes on the hydrogen abstraction by the attack of halogenated methyl radicals, $Cl_3C\cdot$ or $Cl_2HC\cdot$, have been reported⁸⁾ to decrease with the progressive introduction of an electron-withdrawing group on the silicon atom. Kerr *et al.*⁹⁾ reported that the reaction rates of $F_2HC\cdot$ and $FH_2C\cdot$ radicals toward hydrogen abstraction from $HSiCl_3$ were lower than the corresponding rate for $H_3C\cdot$ radicals and explained the result in terms of a polar repulsion between $HSiCl_3$ and the fluorinated methyl radicals. It is clear from the above literature⁶⁻⁹⁾ that the $CH_3\text{-}\underset{O\text{-}SiEt_3}{\dot{C}}\text{-}OCH_3$ and $CH_3\text{-}\dot{C}H\text{-}OCH_3$ radicals in this paper behave like methyl radicals rather than like halogenated methyl radicals.

We attempted the γ-induced reduction of methyl acetate with triethylsilane in tetrachlorosilane, but ethyl methyl ether was not detected by gas chromatography. On the other hand, acetaldehyde dimethyl acetal could be reduced to ethyl methyl ether in a high yield under the same conditions.³⁾ If the adduct, $CH_3\text{-}\underset{O\text{-}Si_3}{CH}\text{-}OCH_3$, were produced, the adduct had to be reduced *via* α-chloroethyl methyl ether¹⁰⁾ to ethyl methyl ether under the same conditions. Consequently, these facts indicate that triethylsilane, containing no chlorine atom, cannot be added to the carbonyl group of methyl acetate.

Experimental

The NMR spectra were recorded on JNM 3H-60, with tetramethylsilane as the external standard. Gas chromatographies were determined by means of a Yanagimoto GCG-5DH, with a 3-m column containing 30% dioctyl phthalate on Celite 545 and using helium as the carrier gas.

Materials. The methoxydichlorosilane (bp 51 °C) was prepared by the methanolysis of trichlorosilane.³⁾ The dimethoxychlorosilane was synthesized in a similar manner: bp 70 °C (lit,¹¹⁾ 70.5 °C).

The other reagents, commercial materials, were previously distilled and stored in an ampoule.

Procedure for γ Irradiation. To an NMR tube which was attached to a vacuum line, given amounts of tetrachlorosilane, methyl acetate, and hydrosilane were transferred successively by means of the vacuum line. Although the procedure on using acetaldehyde dimethyl acetal as a starting material was almost identical with those described above, a hydrosilane was added after the mixture of tetrachlorosilane and the acetal had stood for 30 min. The tube, after being sealed, was irradiated by γ-rays from a ⁶⁰Co source.

Estimation of Products. The adduct was estimated by the use of the NMR intensity of the methyl proton which resulted from the $CH_3C(O)$ in methyl acetate. The results were obtained from the average values of ten scannings. For example, the yield of the addition reaction was calculated by the use of the a/b ratio in Fig. 1, where (a) showed the total methyl intensity of the adduct, α-chloroethyl methyl ether, and ethyl methyl ether, and where (b) gave the sum of (a) and the intensity of the unchanged methyl acetate. The yield of the reduction reaction was estimated in the same manner as above by a comparison of the corresponding methyl intensity of the ether with that of α-chloroethyl methyl ether.

References

1) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).

2) Y. Nagata, T. Dohmaru, and J. Tsurugi, *J. Org. Chem.*, **38**, 795 (1973).

3) R. Nakao, T. Fukumoto, and J. Tsurugi, *ibid.*, **37**, 4349 (1972).

4) The photoinduced decomposition of di-*tert*-butyl peroxide and UV irratiation can initiate the reduction as well as γ irradiation can. However, the use of the peroxide is inconveniently followed by the side reaction of hydrosilane with the acetone produced by the decomposition of the peroxide, and UV irradiation has to be carried out in a quartz NMR tube.

5) An earlier article (B. G. Gowenlock and K. E. Thomas, *J. Chem. Soc.*, **1965**, 5068) has reported an unusually weak $Cl_3Si\text{-}Cl$ bond in tetrachlorosilane, leading to the view that tetrachlorosilane behaves exclusively as a chlorinating agent.

6) J. A. Kerr, D. H. Slater, and J. C. Young, *J. Chem. Soc.*, *A*, **1966**, 104; **1967**, 134.

7) Y. Nagai and H. Sakurai, "Yuriki no Kagaku," Nankodo, Tokyo (1967), p. 246.

8) Y. Nagai, H. Matsumoto, M. Hayashi, E. Tajima, and H. Watanabe, This Bulletin, **44**, 3113 (1971).

9) J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 1 (1971).

10) It was reported that $CH_3\text{-}\underset{O\text{-}SiEt_3}{CH}\text{-}OC_2H_5$ reacted with chlorosilane to give α-chloroethyl ethyl ether in a high yield.³⁾ It is very natural that $CH_3\text{-}\underset{O\text{-}SiEt_3}{CH}\text{-}OCH_3$ is also thought to give α-chloroethyl methyl ether.

11) O. J. Klejnot, *Inorg. Chem.*, **2**, 825 (1963).