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A KINETIC STUDY OF TRICHLOROSILYL RADICAL ADDITION TO ETHYLENE IN THE GAS PHASE

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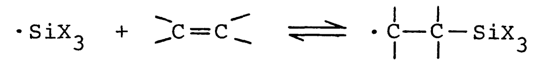
A kinetic study of the photolytic reactions of trichlorosilane with ethylene in the presence of acetone has revealed that the addition of trichlorosilyl radicals to ethylene becomes appreciably reversible around 200°C in the gas phase. ΔH value for the addition of trichlorosilyl radicals to ethylene estimated in this study is about 16 kcal/mol.

Although silyl radical addition reactions to olefins have long been used for the preparation of organosilicon compounds,1) very little kinetic information on these reactions has been available. Also, the reversibility of the silyl radical attachment to olefins as in Eq. (1) has been a subject of great interest but has not given an experimental evidence. Bennett et al. studied the addition of trimethylsilyl radicals to olefins and showed that the reactions were essentially irreversible in solution at temperatures up to 140°C.2) Recently, the detachment of silyl radicals from $\cdot CH_2CH_2SiCl_3$ or $\cdot CH_2CH_2Si(CH_3)_3$ radicals (the reverse of Eq. (1)) was assumed to be important in the thermolysis of ethyltrichlorosilane or ethyltrimethylsilane in the gas phase at 550°C.3)



$$\cdot SiX_3 + {>}C{=}C{<} \rightleftharpoons \cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-SiX_3 \qquad (1)$$

In the present work, we have studied the photolytic reactions of trichlorosilane with ethylene in the presence of acetone in the gas phase between 100° and 275°C in order to obtain a kinetic evidence for the reversibility of reaction (1) and to obtain quantitative informations on the forward and reverse steps involved in the reaction.

Apparatus and procedures are almost similar to those described previously.4) Given amounts of $HSiCl_3$, C_2H_4 and CH_3COCH_3 were admitted into a Pyrex reaction vessel of 18.6 cc which was heated in an electrical oven controlled to better than ±1°C. After the photolysis, the reaction mixture was transferred to a U-shaped cold trap which is directly connected to a gas chromatograph with a Gow-Mac thermister detector.

In a typical experiment, a mixture of 10.8 μmol (18.9 Torr at 250°C) of $HSiCl_3$, 4.3 μmol of C_2H_4 and 10.8 μmol of CH_3COCH_3 was subjected to photolysis for 6 minutes at 250°C. A gaschromatographic analysis of this mixture revealed that the reaction products were almost exclusively $(CH_3)_2CHOSiCl_3$ and $C_2H_5SiCl_3$, the yields of which were 0.38 and 0.13 μmol, respectively. CH_4 and CO were present only as minor products but $H(C_2H_4)_nSiCl_3$ which might arise due to telomerisation,5) was specifically shown to be absent in the present conditions. In all the experiments, the initial amounts of C_2H_4 and CH_3COCH_3 were fixed to be 4.3 and 10.8 μmol, respectively and that of $HSiCl_3$ was varied from 10.8 to 43.3 μmol. Conversions of the reactants were kept smaller than 3%.

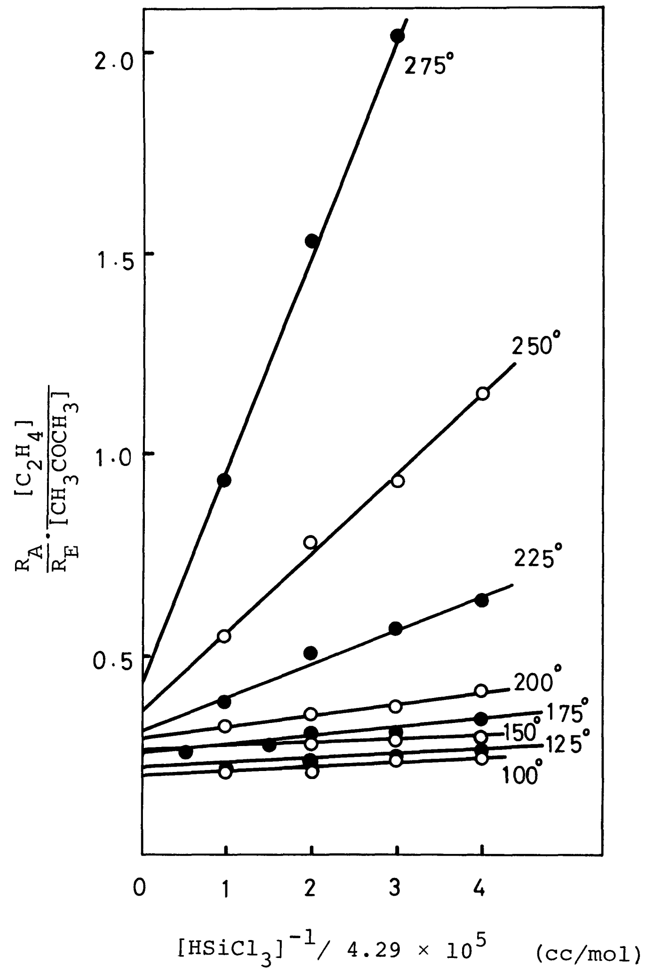


Fig. 1

Plots of data according to Eq. (6). To avoid confusion, data at 100°, 150°, 200° and 250°C were represented by the open circles and those at the other temperatures, by the closed circles.

The photolyses of $HSiCl_3$ - CH_3COCH_3 mixtures[4)] and $HSiCl_3$ - C_2H_4 mixtures[6)] are known to proceed via radical chain reactions involving reactions (2) and (3), and reactions (4) and (5) as chain propagating steps, respectively.

$$\cdot SiCl_3 + (CH_3)_2CO \longrightarrow (CH_3)_2\dot{C}OSiCl_3 \qquad (2)$$

$$(CH_3)_2\dot{C}OSiCl_3 + HSiCl_3 \longrightarrow (CH_3)_2CHOSiCl_3\ (A) + \cdot SiCl_3 \qquad (3)$$

$$\cdot SiCl_3 + C_2H_4 \longrightarrow \cdot CH_2CH_2SiCl_3 \qquad (4)$$

$$\cdot CH_2CH_2SiCl_3 + HSiCl_3 \longrightarrow C_2H_5SiCl_3\ (E) + \cdot SiCl_3 \qquad (5)$$

In the case of $HSiCl_3$ - C_2H_4 - CH_3COCH_3 systems, it may be reasonably assumed that reactions (2) - (5) would be occurring concurrently because the reaction products were almost exclusively A and E.

Under conditions of low conversions of reactants and long reaction chains,[7)] conditions that apply throughout this study, Eq. (6) is derived from the above scheme.

$$\frac{R_A}{R_E} \cdot \frac{[C_2H_4]}{[CH_3COCH_3]} = \frac{k_2}{k_4} \qquad (6)$$

in which R denotes a rate and k does a rate constant. If the reaction (-4), the reverse of the reaction (4), is assumed to be involved in the sequence, then the rate equation may be given by Eq. (7) instead of Eq. (6).

$$\cdot CH_2CH_2SiCl_3 \longrightarrow C_2H_4 + \cdot SiCl_3 \qquad (-4)$$

$$\frac{R_A}{R_E} \cdot \frac{[C_2H_4]}{[CH_3COCH_3]} = \frac{k_2}{k_4} \left(1 + \frac{k_{-4}}{k_5} [HSiCl_3]^{-1} \right) \qquad (7)$$

It may be evident from Eqs. (6) and (7) that the occurrence of the reaction (-4) would be evidenced kinetically by testing the dependency of the rate ratio on $HSiCl_3$ concentrations. The variations in $R_A/R_E \cdot [C_2H_4]/[CH_3COCH_3]$ with $[HSiCl_3]^{-1}$ were examined at various temperatures with $[CH_3COCH_3]/[C_2H_4] = 2.5$. The data were plotted according to Eq. (7) in Fig. 1.

The plots at each temperature give a satisfactory straight line, the intercept of which gives the rate constant ratio, k_2/k_4, and the slope of which divided by the intercept does k_{-4}/k_5. As the magnitude of each slope at lower temperatures (100° - 175°C) is small, it is difficult to evaluate it accurately by experiments. Therefore, the dependency on $HSiCl_3$ concentrations cannot be judged only from these data in this temperature range. However, at 200°C, the rate ratio may be detectably dependent on $HSiCl_3$ concentrations; it follows that the reaction (-4) may be important above 200°C.

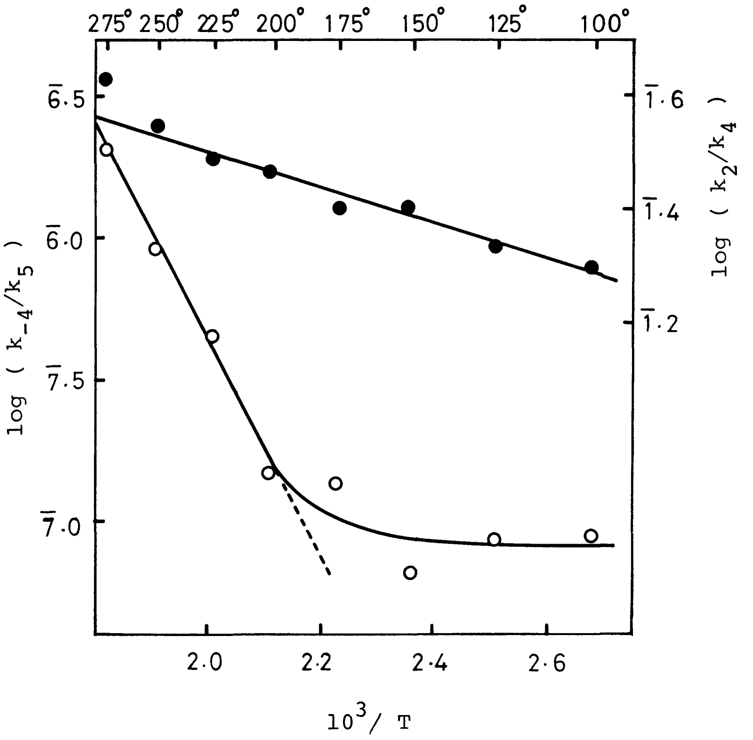


Fig. 2

Arrhenius plots for k_{-4}/k_5 (open circle) and k_2/k_4 (closed circle) calculated from Fig. 1. Arrhenius parameters for k_{-4}/k_5 were estimated between 200° and 275°C where Eq. (7) may be clearly valid.

Arrhenius plots of the rate constant ratios calculated from Fig. 1 are shown in Fig. 2 and the results of least-mean-squares calculations are given in Table 1, where the error limits correspond to the standard deviations.

Table 1 Arrhenius parameters for k_2/k_4 and k_{-4}/k_5 calculated from Fig. 2.

$E_2 - E_4$	1.4 ± 0.1	kcal/mol
$\log(A_2/A_4)$	0.14 ± 0.06	
$E_{-4} - E_5$	18 ± 1	kcal/mol
$\log(A_{-4}/A_5)$	1.3 ± 0.4	mol/cc

As the values of k_5 and E_4 have not been reported, we shall use those of the analogous reactions in order to evaluate ΔH_4, the enthalpy change of the reaction (4). For k_5 we shall adopt the rate constant for the hydrogen abstraction reaction of ethyl radicals from $HSiCl_3$.[8)]

$$\log k_5 \simeq 11.5 - 5.3/\theta \qquad (\text{ mol}^{-1}\text{cc sec}^{-1}) \qquad (8)$$

Then k_{-4} is given as

$$\log k_{-4} \simeq 12.8 - 23.3/\theta \qquad (\text{ sec}^{-1}) \qquad (9)$$

For E_4 we shall use the activation energy of methyl radical addition to C_2H_4.[9)]

$$E_4 \simeq 7 \qquad (\text{ kcal/mol }) \qquad (10)$$

Combining (9) and (10), one can obtain ΔH_4.

$$\Delta H_4 \simeq 16 \qquad (\text{ kcal/mol }) \qquad (11)$$

This value is a little smaller than 18 kcal/mol estimated by Jackson[1)] but agreement may be quite good considering the rough estimations of k_5 and E_4.

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7) The relation $R_2 = R_3$ and $R_4 = R_5$ will hold when the reaction chain is sufficiently long. We previously reported that the chain length was 6 at 100°C in the photolytic addition of trichlorosilane to acetone which involves reactions (2) and (3) as chain propagating steps. Thus, even at 100°C, the lowest temperature in this study, the deviations from $R_2 = R_3$ may not be serious.
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