Kinetics of Gas Phase Addition Reactions of Trichlorosilyl Radicals. VI.[1] Orientation of Additions to 2-Pentenes

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Synopsis. Addition reactions of $\cdot SiCl_3$ radicals to *cis*- and *trans*-2-pentene have been studied in the gas phase between 30 and 136 °C. The ratio of the rate of formation of 2- with 3-trichlorosilylpentane, R_2/R_3, was found to vary with temperature or with $HSiCl_3$ concentrations (1.47—17.6 μmol cm^{-3}). This variation was successfully interpreted by the decomposition of an adduct radical, $CH_3CH(SiCl_3)\dot{C}HCH_2$-$CH_3$.

Quantitative studies of silyl radicals are of general interest now. Previously,[2] we reported that the addition of $\cdot SiCl_3$ radicals to *cis*-2-pentene gave 2- and 3-trichlorosilylpentane (2- and 3-TSP) and that the ratio of formation of the two isomers, R_2/R_3, was 0.47 invariant either with temperature (133—182 °C) or with $HSiCl_3$ concentrations (1.34—5.38 μmol cm^{-3}). It was then found, however, that R_2/R_3 was *ca.* 1.2 in a radiation induced reaction of $HSiCl_3$ with *cis*-2-pentene in cyclohexane at room temperature which was performed to prepare authentic samples of 2- and 3-TSP. It is of interest that the value of R_2/R_3 in the liquid phase is quite different from that in the gas phase. Further, orientation of addition in unsymmetrical olefins may be of importance in relation to the nature of the transition state.[3]

In this connection, we studied the variation of R_2/R_3 with $HSiCl_3$ concentrations and with temperature between 30 and 136 °C to cover the temperature range below that of the previous study.

Experimental

Materials and procedures are essentially similar to those described earlier.[2] Mixtures of CH_3COCH_3, 2-pentene, and $HSiCl_3$ were introduced into a cylindrical Pyrex cell of 137 cm^3 which was heated in an electric oven. The light source was a 50 W medium pressure mercury arc. During this series of experiments, the rate of absorption of light was 7×10^{-12} einstein cm^{-3} min^{-1}. After photolysis, the reaction mixture was passed to a gas sampling loop and was immediately analyzed by GLC.

Results and Discussion

Mixtures of CH_3COCH_3 (2.90 μmol cm^{-3}), $HSiCl_3$ (8.70 μmol cm^{-3}) and *cis*- or *trans*-2-pentene (0.58 μmol cm^{-3}) were photolyzed between 30 and 136 °C in the gas phase. Products were almost exclusively $(CH_3)_2$-$CHOSiCl_3$ (A), 2-, and 3-TSP. The ratio of the rate of formation of the two isomers, R_2/R_3, are shown in Fig. 1 as a function of temperature. R_2/R_3 was *ca.* 1.2 at 30 °C but decreased with an increase in temperature. At 136 °C it agreed with the value of 0.47 previously[2] obtained at higher temperatures. In addition, there was no significant difference in reactivity between *cis*- and *trans*-2-pentene.

The Arrhenius plots of the rate of formation of the respective products are given in Fig. 2.

The plot of log R_A against $1/T$ is seen to be linear; the least-mean-squares treatment of the plot gives

$$\log(R_A/\mu\text{mol cm}^{-3}\text{ min}^{-1}) = 2.52 \pm 0.14 - (2.26\pm0.05)\times10^3/T. \quad (1)$$

In the photolysis of CH_3COCH_3 in the presence of $HSiCl_3$ and 2-pentene, the addition of $\cdot SiCl_3$ radicals to CH_3COCH_3[4] and to 2-pentene[2] is known to constitute chain propagating steps as shown in the following.

$$\cdot SiCl_3 + CH_3COCH_3(Ac) \longrightarrow (CH_3)_2\dot{C}OSiCl_3(\dot{A}) \quad (2)$$

$$\cdot A + HSiCl_3(TCS) \longrightarrow (CH_3)_2CHOSiCl_3(A) + \cdot SiCl_3 \quad (3)$$

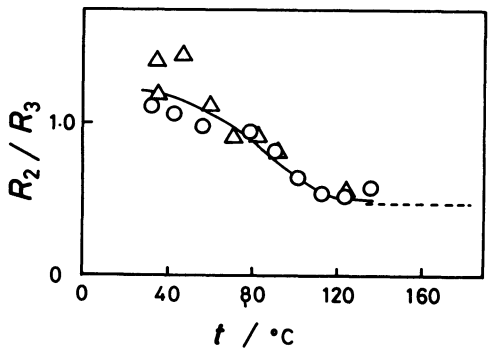

Fig. 1. Variation of R_2/R_3 with temperature.
○: *cis*-Δ^2-C_5H_{10}, △: *trans*-Δ^2-C_5H_{10}, ------: from Ref. 2. [Δ^2-C_5H_{10}]=0.58, [CH_3COCH_3]=2.90, [$HSiCl_3$]=8.70 μmol cm^{-3}.

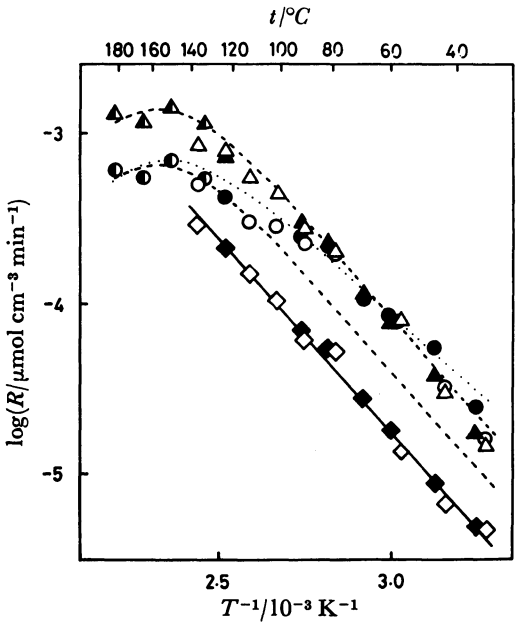

Fig. 2. Arrhenius plots of the rate of formation of the products.
◇: A (Shifted by −0.5), ○: 2-TSP, △: 3-TSP, ◐: 2-TSP from Ref. 2, ◭: 3-TSP from Ref. 2, ------: calculated (see text), ·····: simulation curve based upon Eq. 11. Closed marks are from *trans*-Δ^2-C_5H_{10}.

$$\cdot SiCl_3 + \Delta^2\text{-}C_5H_{10}(P) \rightleftharpoons CH_3\dot{C}HCHCH_2CH_3(\dot{P}_2) \quad (4,-4)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad SiCl_3$$
$$\rightleftharpoons CH_3\dot{C}HCHCH_2CH_3(\dot{P}_3) \quad (4',-4')$$
$$\qquad\qquad\qquad\qquad\quad SiCl_3$$

$$\cdot P_2 + HSiCl_3 \longrightarrow 2\text{-TSP} + \cdot SiCl_3 \quad (5)$$

$$\cdot P_3 + HSiCl_3 \longrightarrow 3\text{-TSP} + \cdot SiCl_3 \quad (5')$$

Chain terminating radicals are probably[4] $\cdot A$, $\cdot P_2$, and $\cdot P_3$. Irreversibility of reaction (2) up to 253 °C has already been shown[4] in this laboratory.

In the scheme above, three chain cycles resulting in the adducts A, 2-, 3-TSP occur concurrently. Assuming low conversions of the reactants and long reaction chains, one obtain the following rate equations by the conventional steady state treatment.

$$R_2/R_A = ([P]/[Ac])(k_4/k_2)\{1+(k_{-4}/k_5)[TCS]^{-1}\}^{-1}, \quad (6)$$

$$R_3/R_A = ([P]/[Ac])(k_{4'}/k_2)\{1+(k_{-4'}/k_{5'})[TCS]^{-1}\}^{-1}, \quad (6')$$

where R_2, R_3, and R_A denote the rates of formation of 2-, 3-TSP, and A, respectively.

Recently,[2] we obtained the following rate constant ratios for *cis*-2-pentene between 133 and 182 °C using Eqs. 6 and 6'.

$$\log(k_4/k_2) = 0.57,\ \log(k_{4'}/k_2) = 0.89$$

$$\log(k_{-4}/k_5) = 5.39 - 20500/2.3\,RT(\text{mol cm}^{-3}),$$

and $$\log(k_{-4'}/k_{5'}) = \log(k_{-4}/k_5). \quad (7)$$

Based upon these values, Eqs. 6, 6', and 1 allow the values of $\log R_2$ and $\log R_3$ to be calculated in the extended temperature range. These calculated values are illustrated in Fig. 2 as dotted lines. It is interesting to note that while $\log R_3$ agrees with the dotted line over the temperature range adopted, $\log R_2$ behaves quite differently with the extended value especially at low temperatures.

The results in Fig. 2 imply that the change in orientation of addition illustrated in Fig. 1 may be caused only by the change in R_2.

Another series of experiments was carried out to ascertain this implication. With other conditions being kept constant, the dependence of the rate of formation of the products on $HSiCl_3$ concentrations was studied at 61 °C. The results are shown in Fig. 3. To check the third body effect, 17.6 μmol cm^{-3} of CO_2 was added at $[HSiCl_3]=1.47$ μmol cm^{-3}, but there was almost no effect.

The results in Fig. 3 show that the variation of $[HSiCl_3]$ has almost no effect on R_3/R_A but has strong effect on R_2/R_A. This fact suggests that some reactions eliminating $\cdot P_2$ radicals compete with reaction (5). The most probable reactions as such are (8), (9), and (−4).

$$\cdot P_2 + \cdot R(\text{any radicals}) \longrightarrow \text{products} \quad (8)$$

$$\cdot P_2 + P \longrightarrow \text{telomer} \quad (9)$$

Reaction (8) is indeed occurring as one of the terminating reactions. But the kinetic chain length of reaction (5) is estimated to be >10 in this experiment, *i.e.*, $R_8/R_2<0.1$, so reaction (8) cannot contribute to the change in R_2 to such an extent as is shown in Fig. 3.

Since $\cdot P_2$ is more reactive than $\cdot P_3$ (stabilized by CH_3–) or $\cdot A$ (tertiary radical), reaction (9) may be reasonably assumed more important than the similar

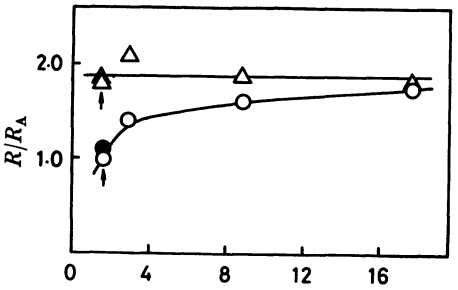

Fig. 3. Dependence of R_2/R_A and R_3/R_A on $HSiCl_3$ concentrations.
△: R_3/R_A, ○: R_2/R_A, ▲, ●: 17.6 μmol cm^{-3} of CO_2 was added. ↑: Formation of *trans*-Δ^2-C_5H_{10} was checked in this run. [*cis*-Δ^2-C_5H_{10}]=0.58, [CH_3COCH_3]=2.90 μmol cm^{-3}.

telomerization reactions involving $\cdot P_3$ or $\cdot A$. When reaction (9) is tentatively included in the mechanism, R_2/R_A is derived as in Eq. 10.

$$R_2/R_A = ([P]/[Ac])(k_4/k_2)\{1+(k_{-4}/k_5)[TCS]^{-1} + (k_9/k_5)([P]/[TCS])\}^{-1} \quad (10)$$

The result in Fig. 3 could be interpreted in terms of Eq. 10 if $k_9/k_5=2.5$ at 61 °C were assumed. But this ratio is clearly too large because alkyl radicals abstract H atoms from $HSiCl_3$[5] faster than they add to alkenes.[6]

Reaction (−4) would accompany *cis-trans* isomerization of 2-pentene. Under the condition indicated in Fig. 3, we checked the formation of *trans*-2-pentene and found that *cis-trans* rearrangement occurred ($R_{trans}=2.3\times10^{-4}$ μmol cm^{-3} h^{-1}) to the extent comparable to the difference between R_3 and R_2 ($R_3-R_2=3.8\times10^{-4}$ μmol cm^{-3} h^{-1}). Without $HSiCl_3$, however, the isomerization occurred ($R_{trans}=1.4\times10^{-4}$ μmol cm^{-3} h^{-1}) as might be expected from the study by Cundall and Davies.[7] Comparison of the rates of isomerization with and without $HSiCl_3$, shows clearly that $\cdot SiCl_3$ radicals enhance isomerization.

Based upon the fact that $\cdot P_2$ radicals decompose at moderate temperatures the values of k_{-4}/k_5 and k_4/k_2 were obtained by iterative calculation to satisfy the result in Fig. 2 (trial and error calculations were made).

$$\log(k_{-4}/k_5) = 4.89 - 19500/2.3\,RT$$

$$\log(k_4/k_2) = -0.54 + 2190/2.3\,RT \quad (11)$$

The curve for $\log R_2$ based upon Eq. 11 is shown in Fig. 2.

References

1) Part V: T. Dohmaru and Y. Nagata, *J. Phys. Chem.*, **86**, 4522 (1982).

2) T. Dohmaru and Y. Nagata, *J. Chem. Soc., Faraday Trans. 1*, **78**, 1141 (1982).

3) J. M. Tedder and J. C. Walton, *Acc. Chem. Res.*, **9**, 183 (1976).

4) T. Dohmaru, Y. Nagata, and J. Tsurugi, *Bull. Chem. Soc. Jpn.*, **45**, 2660 (1972).

5) N. L. Arthur and T. N. Bell, *Rev. Chem. Intermediates*, **2**, 37 (1978).

6) J. M. Tedder and J. C. Walton, "Advances in Physical Organic Chemistry," ed by V. Gold and D. Bethell, Academic Press, London (1978), Vol. 16, p. 51.

7) R. B. Cundall and A. S. Davies, *Proc. R. Soc. London, Ser. A*, **290**, 563 (1966).