

Kinetics of Gas Phase Addition Reactions of Trichlorosilyl Radicals. IV.¹⁾ Relative Rates of Additions to 1-Alkenes

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Synopsis. Trichlorosilyl radical additions to a mixture of ethene, propene, 1-butene, and 1-pentene and to a mixture of propene and 2-methylpropene have been investigated. The rate of adduct formation from each olefin was obtained relative to that from propene between 403 K and 548 K. These relative rates are in good agreement with those calculated from the rate parameters obtained previously in this laboratory.

Kinetic data relating to elementary reactions of silyl radicals are quite important since reliable thermochemical or kinetic informations are now still very scarce.

Previously,²⁾ we obtained Arrhenius parameters for forward and reverse steps of $\cdot\text{SiCl}_3$ additions to 1-alkenes between 405 K and 524 K by a competitive method in which an addition to acetone was employed as a reference reaction. To check the reliability of these results and to obtain precise relative rates of additions to 1-alkenes, we conduct a series of experiments in which mixtures of 1-alkenes are subjected to reactions with $\cdot\text{SiCl}_3$ radicals.

Experimental

The materials were prepared, purified and checked in the way described previously.²⁾ Sample preparations and photolyses were performed on a conventional greaseless and mercury-free vacuum line. The full light from a 50 W medium pressure mercury arc was used. Given amounts of HSiCl_3 and a mixture of olefins were admitted into a quartz reaction vessel of 139 cm³ which was heated in an electrical oven controlled to better than ± 1 K. Probably very weak photoabsorption by olefins in the ultraviolet region initiates the reactions, since HSiCl_3 was found almost transparent in this region. After photolyzed, the reaction mixture was allowed to diffuse to a gas sampling loop which was directly attached to a gas chromatograph with a Gow-Mac gas density detector. All the analyses were made on a 2 m column of 30% SE 30 on Chromosorb W mixed with 30% Silicone DC QF-1 on Chromosorb W (1:1 by weight). Reactant conversions were kept smaller than 5%.

Results and Discussion

Equimolar mixtures of ethene, propene, 1-butene and 1-pentene (0.267×10^{-6} mol cm⁻³ each) were photolyzed in the presence of HSiCl_3 (5.34×10^{-6} mol cm⁻³). Products were $\text{C}_2\text{H}_5\text{SiCl}_3$, $n\text{-C}_3\text{H}_7\text{SiCl}_3$, $n\text{-C}_4\text{H}_9\text{SiCl}_3$, and $n\text{-C}_5\text{H}_{11}\text{SiCl}_3$; additions occur exclusively at their terminal carbons. Since it was difficult to separate $i\text{-C}_4\text{H}_9\text{SiCl}_3$ completely from $n\text{-C}_4\text{H}_9\text{SiCl}_3$ in gas chromatographic analyses, 2-methylpropene was subjected to another photolysis in which propene and 2-methylpropene (0.134×10^{-6} mol cm⁻³ each) were photolyzed with HSiCl_3 (5.34×10^{-6} mol cm⁻³). In both series of photolyses, the amounts of the products were measured at various temperatures

TABLE 1. RELATIVE RATES OF ADDITIONS OF HSiCl_3 TO 1-ALKENES

T/K	C_2H_4	C_3H_6	$\Delta^1\text{-C}_4\text{H}_8$	$\Delta^1\text{-C}_5\text{H}_{10}$	$i\text{-C}_4\text{H}_8$
403	0.27	1	1.1	1.0	4.1
428	0.32	1	1.1	1.2	4.1
452	0.34	1	1.1	1.1	3.0
477	0.39	1	1.2	1.0	2.0
501	0.52	1	1.1	0.9	1.3
525	0.85	1	1.1	1.0	1.0
548	1.1	1	1.2	1.0	0.8

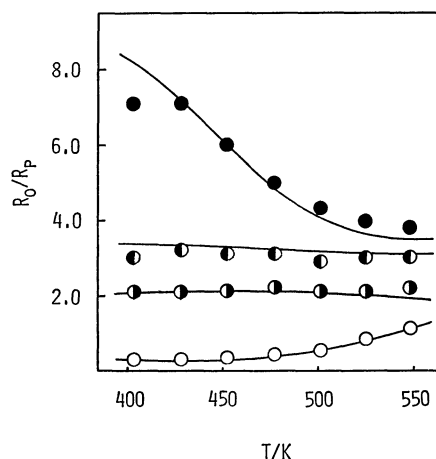


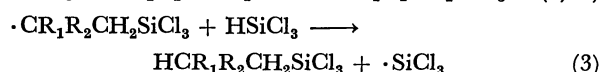
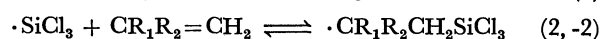
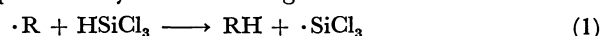
Fig. 1. Observed and calculated relative rates of addition between 403 K and 548 K.

○: C_2H_4 , ◐: $\Delta^1\text{-C}_4\text{H}_8$ (shifted by +1), ◑: $\Delta^1\text{-C}_5\text{H}_{10}$ (shifted by +2), ●: $i\text{-C}_4\text{H}_8$ (shifted by +3)
The solid curves represent the calculated values.

between 403 K and 548 K. The results are summarized in Table 1.

Features characteristic of the number of the alkyl substituents around the double bond are clear in Table 1. Monosubstituted ethenes (C_3H_6 , $\Delta^1\text{-C}_4\text{H}_8$, and $\Delta^1\text{-C}_5\text{H}_{10}$) are very similar in reactivity with each other throughout the temperature range. Ethene has a small rate at low temperature but gets to the same rate as that of propene at 548 K. 2-Methylpropene behaves in a quite opposite way to ethene. It is quite interesting to note that each relative rate attains almost the same value at about 530 K.

The photolytic addition of HSiCl_3 to olefin is known to proceed by the following radical chain reactions.³⁾



$\cdot\text{R}$ in Reaction 1 represents any radicals formed as a result of photoabsorption by some olefins.

The rate of the formation of the respective adduct, R_o , is derived as in Eq. 4 applying the steady state treatment of the above scheme; the conditions of long reaction chains and low conversion of reactants are satisfied in the present runs.²⁾

$$R_o = \frac{k_2[\text{Olefin}][\cdot\text{SiCl}_3]}{1 + (k_{-2}/k_3)[\text{HSiCl}_3]^{-1}} \quad (4)$$

We have already obtained rate constant ratios k_2/k_5 and k_{-2}/k_3 for 1-alkenes where k_5 denotes the rate constant of the $\cdot\text{SiCl}_3$ addition to acetone.²⁾ Accordingly, the relative rates of adduct formations among olefins can be calculated from Eq. 4. The rates of adduct formation from the respective olefin, R_o , relative to that from propene, R_p , are compared with

the calculated values at various temperatures in Fig. 1. The experimental rate ratios are in good agreement with the calculated values; the present study lends support to the rate parameters obtained previously.²⁾

References

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 - 2) T. Dohmaru and Y. Nagata, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2617 (1979).
 - 3) T. Dohmaru, Y. Nagata, and J. Tsurugi, *Chem. Lett.*, **1973**, 1031.
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