

## Kinetics of Addition of 2-Methyl-2-silapropene to Methyl Trimethylsilyl Ether

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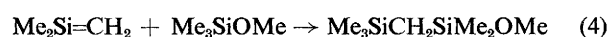
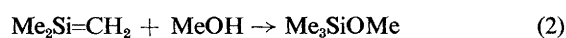
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Arrhenius parameters for the regiospecific addition of  $\text{Me}_2\text{Si}=\text{CH}_2$  across the silicon–oxygen bond in  $\text{Me}_3\text{SiOMe}$ , giving  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{OMe}$ , have been measured; comparisons are made with similar reactions.

Although there is considerable current interest in the chemistry of silaethene intermediates, kinetic studies of their reactions are rare. Data have only been obtained for the gas phase addition of 2-methyl-2-silapropene (SE) to hydrogen halides and oxygen<sup>1</sup> and for the reaction of SE with some olefins, *e.g.* propene.<sup>2</sup>

SE is known to react with alcohols, ROH, to form trimethylsilyl ethers,  $\text{Me}_3\text{SiOR}$ ,<sup>3–8</sup> by addition across the hydrogen–oxygen bond. Similarly, addition across the silicon–oxygen bond in the cyclic compound  $(\text{Me}_2\text{SiO})_3$  gives a ring expansion product.<sup>9</sup> In a recent study<sup>7</sup> on the addition of SE, generated by thermolysis of 1,1-dimethyl-1-silacyclobutane (DMSCB), to methanol, secondary regiospecific addition of SE to the primary product, methyl trimethylsilyl ether, was observed [reaction (4) in Scheme 1].

Our original intention was to measure the kinetics of reaction (2), using our low-pressure pyrolysis (LPP) tech-



Scheme 1

nique,<sup>10</sup> as in our earlier work on the additions of SE to hydrogen halides and oxygen.<sup>1</sup> Although the DMSCB–methanol copyrolysis experiments followed the expected course [reactions (1) to (3)], reaction (4) was significant and reaction (2) was too fast to be measured satisfactorily by our technique in its present form. However, the LPP technique was suitable for measuring the kinetics of reaction (4) by

pyrolysing DMSCB in the presence of methyl trimethylsilyl ether itself.  $^1\text{H}$  N.m.r. analysis of the product, resulting from combining the reaction mixture of several copyrolyses, gave identical results to those of John *et al.*,<sup>7</sup> so we confirm their conclusions as to the regiospecific nature of the addition process. (It is noted that the same product could be obtained by addition to the silicon-methyl, instead of the silicon-oxygen, bond, but we consider this unlikely.) No evidence was found for any other addition and no further addition to the product was observed under LPP conditions. In a reaction vessel pre-conditioned by pyrolysis of neat DMSCB the only other products observed were traces ( $<0.1\%$ ) of the cyclic compounds  $(\text{Me}_2\text{SiO})_3$ ,  $(\text{Me}_2\text{SiO})_2\text{Me}_2\text{SiCH}_2$ , and  $\text{Me}_2\text{SiO}(\text{Me}_2\text{SiCH}_2)_2$ .

Quantitative measurements were done using a mixture of DMSCB and methyl trimethylsilyl ether in the ratio 1:2, which was pyrolysed at temperatures between 732 and 789.5 K, initial pressures being *ca.* 0.3 mmHg. The normal kinetic method of measuring  $k_4$  relative to  $(k_3)^{\frac{1}{2}}$  was used, the formation of  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{OMe}$  being taken as a measure of the rate of reaction (4). If we assume  $k_3 = 10^{4.55} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

with zero activation energy<sup>11</sup> then our results give  $\log_{10} k_4/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (5.3 \pm 0.2) - (6.3 \pm 3.2 \text{ kJ mol}^{-1})/2.303RT$ .

Further experiments were done in which a series of pyrolyses were carried out using different mixture compositions, ranging from 4:1 to 1:6 (DMSCB:methyl trimethylsilyl ether) and extended temperature ranges, 725 to 825 K, confirming the above results. The Arrhenius parameters are compared with those for similar reactions in Table 1.

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**Table 1.** Arrhenius parameters for silaethene addition (relative to  $k_3 = 3.55 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

Reactants	$\log_{10} A$	$E/\text{kJ mol}^{-1}$	$k(800 \text{ K})$
$\text{Me}_2\text{Si}=\text{CH}_2 + \text{Me}_3\text{SiOMe}^a$	$5.3 \pm 0.2$	$6.3 \pm 3.2$	$7.7 \times 10^4$
$\text{Me}_2\text{Si}=\text{CH}_2 + \text{HCl}^b$	$7.5 \pm 0.5$	$10 \pm 7$	$7.0 \times 10^6$
$\text{Me}_2\text{Si}=\text{CH}_2 + \text{O}_3^b$	$7.6 \pm 0.3$	$15 \pm 5$	$4.2 \times 10^6$
$\text{Me}_2\text{Si}=\text{CH}_2 + \text{HBr}^b$	$7.4 \pm 0.5$	$36 \pm 7$	$1.1 \times 10^5$
$\text{Me}_2\text{Si}=\text{CH}_2 + \text{C}_3\text{H}_6^c$	$5.2 \pm 0.6$	$35 \pm 4$	$8.2 \times 10^2$

<sup>a</sup> This work. <sup>b</sup> Ref. 1. <sup>c</sup> Ref. 2.