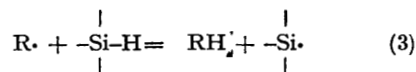
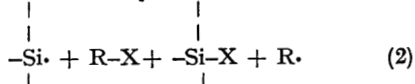
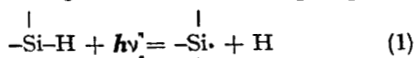


## Reactions of Trichlorosilyl Radicals with Alkyl Chlorides

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HASZELDINE and YOUNG<sup>1</sup> suggested that a chain reaction occurs when a silane is photolysed in the presence of an organic halide in the liquid phase,



where X is a halogen atom and R a substituted alkyl radical.

We have investigated this reaction in the gas phase, and find that the trichlorosilyl radical, produced by the irradiation of trichlorosilane with

ultraviolet light, extracts a chlorine atom from simple alkyl chlorides. No products were detected to suggest any reaction of the alkyl radical other than Reaction 3 above. There was no dark

step. The ratio of rate constants has been measured over the temperature ranges quoted when R is isopropyl, and activation energy differences found from Arrhenius plots. The ratio

TABLE

*Relative reactivity of alkyl halides with the trichlorosilyl radical*

R*	Temp. range	$\frac{A(\text{Pr}^1)}{A(\text{R}^*)}$	$E(\text{R}^*) - E(\text{Pr}^1)$ kcal. mole <sup>-1</sup>	$D(\text{C}-\text{Cl})^3$	$\frac{k(\text{Pr}^1)}{k(\text{R}^*)}$ at 275° SiCl <sub>3</sub>	at Na <sup>2</sup>
Et	113—248°	1.06	0.75	81.5	3.56	2.1
Bu <sup>n</sup>	97—263	1.22	0.64	—	2.18	1.0
Bu <sup>i</sup>	97—293	1.46	0.56	—	2.43	1.1
Me <sub>3</sub> C·CH <sub>3</sub>	88—252	1.79	0.42	—	2.63	—
Bu <sup>s</sup>	129—263	0.90	0.10	81	0.82	0.7
Bu <sup>t</sup>	77—190	1.05	-1.39	78.5	0.30	0.45

reaction. As the product of Reaction 3 is a simple alkane that can be estimated by gas chromatography, its estimation provides a method of measuring the rate-determining abstraction of chlorine.

Relative rates of reaction of two alkyl chlorides, RCl and R\*Cl have been measured by competitive experiments. The ratio  $k_2(\text{RCl})/k_2(\text{R}^*\text{Cl})$  was found to be independent of the initial concentrations of RCl and R\*Cl over a range of concentration ratios  $[\text{RCl}]/[\text{R}^*\text{Cl}]$  between 0.3 and 10.0, thus confirming that Reaction 2 is the rate-determining

of *A*-factors is approximately unity for all pairs, so rate differences can be largely attributed to differences of activation energies. For the sake of comparison ratios of rate constants obtained for the analogous sodium flame reactions<sup>2</sup> are quoted.

It can be seen that, as can be expected from consideration of the respective carbon-chlorine bond dissociation energies, the activation energies decrease in the order: primary (C-Cl) > secondary (C-Cl) > tertiary (C-Cl).

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<sup>1</sup> R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, 1960, 4503.

<sup>2</sup> H. v. Hartel, N. Meer, and M. Polanyi, *Z. phys. Chem.*, 1932, 19, B, 139.

<sup>3</sup> S. W. Benson, *J. Chem. Educ.*, 1965, 42, 502.