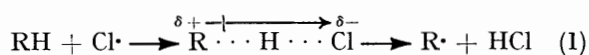


## Free Radical Substitution in Aliphatic Compounds. Part XXIX.<sup>1</sup> Halogen Atom Abstraction from Alkyl Halides by Trimethyltin Radicals in the Gas Phase

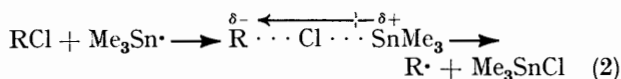
By David A. Coates and John M. Tedder,\* Department of Chemistry, The Purdie Building, The University, St. Andrews KY16 9ST

Mixtures of trimethyltin hydride and halogenoalkanes have been irradiated in the gas phase by a medium pressure mercury lamp. A very rapid reaction ensues in which a halogen atom in the original halogenoalkane is displaced by a hydrogen atom and trimethyltin halide is formed. The reaction is interpreted as a chain process involving halogen abstraction by trimethyltin radicals. Competitive experiments have been carried out and in general the reaction is very unselective: the different halogens are abstracted from similar sites in the order Br > Cl > F and the reactivity of different sites lies in the order tertiary > secondary > primary. The relative rates of chlorine abstraction from a series of molecules with the formula RCl<sub>3</sub> has been determined. If R is electron attracting, chlorine abstraction is facilitated and if R is electron repelling chlorine abstraction is retarded. These results are considered to be evidence of a polar effect exactly opposite to that observed in reactions involving hydrogen abstraction by chlorine atoms.

PREVIOUS papers in this series have been mainly concerned with free radical substitution resulting from hydrogen abstraction by halogen atoms or by alkyl radicals. In Parts IX—XI<sup>2</sup> halogen abstraction by hydrogen atoms was investigated but the method employed did not prove suitable for an investigation of directive effects in halogen abstraction. The present work was initiated with the intention of obtaining further information about halogen abstraction and particularly about polar effects. In order to account for the observed directive effects in hydrogen abstraction reactions most authors have assumed that the activated complex has considerable polar character with the halogen forming the negative end of the dipole [reaction (1)].<sup>3-5</sup> In halogen abstraction by trimethyltin radicals



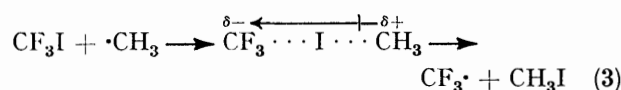
we would expect the polarisation to be reversed [reaction (2)]. If chlorine atoms can be abstracted by



trimethyltin radicals from the same sites that hydrogen atoms have been abstracted by halogen atoms, direct confirmation (or refutation) of the polar concepts should be obtained.

Previous work on halogen abstraction includes work involving aryl radicals,<sup>6</sup> alkyl radicals,<sup>7-9</sup> trifluoromethyl radicals,<sup>10</sup> and trichlorosilyl radicals.<sup>11</sup> The last work is the most similar to the present investigation, but some comment about the work of Szwarc and his co-workers<sup>7</sup> (using methyl radicals) and of Alcock

and Whittle<sup>10</sup> (using trifluoromethyl radicals) is necessary. Both these groups draw attention to the fact that methyl radicals and trifluoromethyl radicals preferentially abstract hydrogen atoms in cases where simple bond strength arguments would lead one to expect halogen atom abstraction to be preferred. Szwarc *et al.* suggest that this relative facility for hydrogen abstraction is due to the presence of coulombic repulsion between the *p* electron of the attacking radical and the closed shell of the halogen atom. Szwarc also invokes this repulsion concept to explain the fact that even though *D*(CF<sub>3</sub>-I) is slightly greater than *D*(CH<sub>3</sub>-I) abstraction of iodine from trifluoromethyl iodide is about 500 times faster at 338 K than abstraction from methyl iodide. This latter result as Szwarc *et al.* observe can also be explained in terms of a simple polar argument in which the transition state can be represented as in reaction (3) but they prefer to consider the effect



the electronegative trifluoromethyl group will have on the supposed Coulombic repulsion. The same phenomenon also arises with bromotrichloromethane and benzyl bromide where the methyl radical abstracts bromine from the halogenomethane faster than from the benzyl bromide.

In the reaction of trialkyltin radicals with partially halogenated alkanes, hydrogen abstraction is thermodynamically less favourable than halogen abstraction so that regardless of the interpretations of the data

<sup>1</sup> Part XXVIII, D. S. Ashton, J. M. Tedder, M. Walker, and J. C. Walton, *J.C.S. Perkin II*, 1973, 1346.

<sup>2</sup> D. T. Clark and J. M. Tedder, *Trans. Faraday Soc.*, 1966, **62**, 393, 399, 405.

<sup>3</sup> C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1967, pp. 347 *et seq.*

<sup>4</sup> J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336.

<sup>5</sup> W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, pp. 170 *et seq.*

<sup>6</sup> D. H. Hey and J. Peters, *J. Chem. Soc.*, 1960, 79, 88; D. H. Hey, and R. Tewfik, *ibid.*, p. 2402; J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *ibid.*, 1965, 3939, 3950.

<sup>7</sup> F. W. Evans, R. J. Fox, and M. Szwarc, *J. Amer. Chem. Soc.*, 1960, **82**, 6414; F. W. Evans and M. Szwarc, *Trans. Faraday Soc.*, 1961, **57**, 1905; R. J. Fox, F. W. Evans, and M. Szwarc, *ibid.*, p. 1915.

<sup>8</sup> D. M. Tomkinson, J. P. Galvin, and H. O. Pritchard, *ibid.*, 1964, **68**, 541; D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, 1966, **70**, 1579.

<sup>9</sup> K. D. King and E. S. Swinbourne, *Austral. J. Chem.*, 1965, **18**, 121; *J. Phys. Chem.*, 1967, **71**, 2371.

<sup>10</sup> W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244, 866; 1965, **62**, 134.

<sup>11</sup> J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc. (A)*, 1968, 510.

of ref. 7 we would expect halogen abstraction to predominate.

Halogen abstraction by trialkyltin radicals has been extensively investigated by Kuivila and his co-workers.<sup>12</sup> More recently Ingold and his co-workers<sup>13</sup> have made a number of kinetic studies involving the same reaction. Both these groups examined the liquid-phase reaction, and very little data relating to the gas-phase reactions of these radicals have been reported. The most similar study to the present work is that of Kerr *et al.*<sup>11</sup> who studied the gas-phase abstraction of halogen atoms from alkyl halides with trichlorosilyl radicals.

#### EXPERIMENTAL

*Materials.*—Trimethyltin hydride was prepared by treatment of trimethyltin chloride with lithium aluminium hydride in di-*n*-butyl ether.<sup>14</sup> The product was purified by distillation to yield trimethyltin hydride of >98% purity (the main impurity was tetramethyltin together with traces of some lower boiling component, probably dimethyltin dihydride) and stored in a nitrogen atmosphere at  $-15^{\circ}\text{C}$ . 1-Chloro-4-fluorobutane was synthesised from 1,4-dichlorobutane.<sup>15</sup> 1,3-Dichloro-3-methylbutane was prepared from isoprene and hydrogen chloride<sup>16</sup> and 1-bromo-4-chlorobutane from 4-chlorobutanol.<sup>17</sup> The remaining alkyl halides were from commercial sources and all were purified by preparative g.l.c. when necessary.

*Method.*—A conventional vacuum line was employed. The quartz reaction vessel ( $133 \pm 1.1 \text{ cm}^3$ ) was cylindrical with plane quartz windows at each end. The vessel was irradiated with a Hanovia U.V.S. 220 medium pressure mercury arc placed  $13.5 \pm 0.2 \text{ cm}$  from the reaction window.

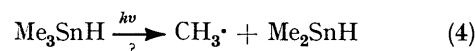
Quantitative analysis was effected on a Griffin and George D6 gas chromatograph in which the detector was a James and Martin gas density balance and peak areas were measured on a Dupont 310 curve resolver. The products were identified by comparison of their retention times with those of authentic samples and in some cases from their mass spectra produced by g.l.c.–mass spectrometry.

The reaction times were adjusted to achieve a 5% conversion of the trimethyltin hydride. Only in the reaction with 1-bromo-4-chlorobutane was this greatly exceeded [see Table 1(i)].

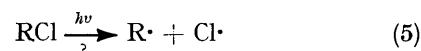
#### DISCUSSION

The radical nature of the 'reduction' of alkyl halides by organotin hydrides was established by Menapace and Kuivila.<sup>12</sup> Confirmation of a radical chain mechanism is provided by the work of Carlsson and Ingold.<sup>13</sup> In the present work the reaction occurs in the gas phase and requires u.v. light to initiate the process. Taken together with the earlier work there can be no doubt that the present reactions involve a radical chain

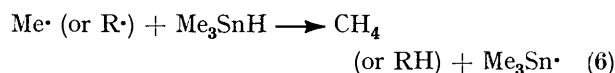
mechanism. The exact nature of the initiation step has yet to be elucidated. Two possibilities fit the observations, either the fission of carbon–tin bond (rather than a hydrogen–tin bond) of trimethyltin hydride [reaction (4)] or possibly fission of a carbon–halogen



bond in the alkyl halide [reaction (5)]. No reaction was observed in a Pyrex reaction vessel and therefore



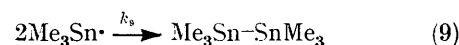
the effective radiation must be the 2537 Å mercury line. Neither the trimethyltin hydride nor the majority of the alkyl halides studied absorb strongly in this region and initiation must be attributed to end absorption. The similarity in conditions required for different alkyl halides suggests that reaction (4) rather than reaction (5) is principally involved. The photolysis step (4) or (5) will be followed by reaction (6) of the radical so produced with trimethyltin hydride.



Although uncertainty remains as to the exact nature of the photolysis, the chain-carrying steps are (7) and (8).



The half-power light dependency and the isolation of hexamethylditin suggest that combination (9) of two trimethyltin radicals is the predominant chain



termination process. The extent of reaction for very short reaction times argues for very long chains. Since neither reaction (7) or (8) are likely to be reversible under the experimental conditions employed, for conversions of 10% or less we can express the relative rates of chlorine abstraction from two different sites RCl and R'Cl in a competitive reaction by equation (10)

$$\frac{k_7}{k'_7} = \frac{[\text{RH}]_f[\text{R}'\text{Cl}]_i}{[\text{R}'\text{H}]_f[\text{RCl}]_i} \quad (10)$$

where subscripts i and f stand for initial and final concentrations respectively.

It is interesting to compare the thermochemistry<sup>18</sup> of reactions (7) and (8) with the thermochemistry of

<sup>12</sup> H. G. Kuivila, L. W. Manapace, and C. R. Warner, *J. Amer. Chem. Soc.*, 1964, **86**, 3047; H. G. Kuivila and L. W. Manapace, *J. Org. Chem.*, 1963, **28**, 2165; C. R. Warner, R. J. Strunk, and H. G. Kuivila, *ibid.*, 1966, **31**, 3381.

<sup>13</sup> D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1962, **90**, 7047; D. J. Carlsson, K. U. Ingold, and L. C. Bray, *Internat. J. Chem. Kinetics*, 1969, **1**, 315.

<sup>14</sup> G. I. M. van der Kerk, J. G. Noltes, and J. G. A. Linzten, *J. Appl. Chem.*, 1957, **7**, 366.

<sup>15</sup> F. W. Hoffmann, *J. Org. Chem.*, 1950, **15**, 425.

<sup>16</sup> I. Kondakov, *J. Russ. Phys. Chem. Soc.*, 1892, **29**, 1513.

<sup>17</sup> J. B. Clark, R. J. Anderson, J. Lackmann, and G. E. Smith, *J. Amer. Chem. Soc.*, 1931, **53**, 2991.

<sup>18</sup> R. A. Jackson, *Adv. Free Radical Chem.*, 1969, **3**, 231.

TABLE I

## Competitive reactions; product ratios (mean of five or more analyses)

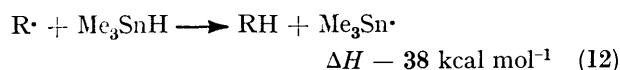
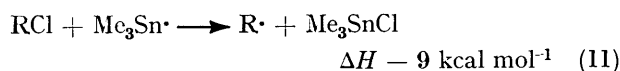
The alkyl halide concentrations were  $3.32 \times 10^{-4}M$  and the trimethyltin hydride concentration  $7.76 \times 10^{-4}M$ . The products  $Me_3SnCl$ ,  $Me_3Sn_2$ , and the 'reduced alkyl' halides were identified by comparison of their retention times with those of authentic specimens

(a) 2-Chloropentane: 1-chloroheptane (reaction time 600 s)									
Temp. (°C)	165	152	114	78	55	44			
$[n-C_7H_{14}] / [n-C_5H_{12}]$	$1.71 \pm 0.01$	$1.58 \pm 0.01$	$1.21 \pm 0.01$	$0.72 \pm 0.01$	$0.44 \pm 0.01$	$0.60 \pm 0.03$			
(b) 1,3-Dichlorobutane (reaction time 600 s)									
Temp. (°C)	161	128	114	85	65	50	41	36	
$[1-ClC_4H_9] / [2-ClC_4H_9]$	$1.18 \pm 0.05$	$2.50 \pm 0.04$	$2.47 \pm 0.04$	$2.54 \pm 0.14$	$3.07 \pm 0.08$	$3.30 \pm 0.10$	$2.38 \pm 0.14$	$3.12 \pm 0.05$	
(c) 1,3-Dichlorobutane: chlorocyclohexane (reaction time 600 s)									
Temp. (°C)	155	139	125	117	85	70	65	40	28
$[cyclo-C_6H_{12}] / [1-ClC_4H_9]$	$2.52 \pm 0.07$	$2.05 \pm 0.01$	$2.34 \pm 0.11$	$1.59 \pm 0.04$	$2.43 \pm 0.37$	$2.04 \pm 0.23$	$1.57 \pm 0.01$	$1.98 \pm 0.02$	$1.18 \pm 0.12$
(d) 1,3-Dichloro-3-methylbutane: chlorocyclohexane (reaction time 600 s)									
Temp. (°C)	145	113	89	75	68	35			
$[cyclo-C_6H_{12}] / [2-Cl, 2-MeC_4H_9]$	$4.28 \pm 0.03$	$2.52 \pm 0.10$	$2.47 \pm 0.32$	$2.41 \pm 0.17$	$2.24 \pm 0.17$	$1.98 \pm 0.02$			
(e) 2,5-Dichloro-2-methylbutane (reaction time 600 s)									
Temp. (°C)	162	146	111	90	60	49	33		
$[2-Cl, 3-MeC_4H_9] / [2-Cl, 2-MeC_4H_9]$	$14.83 \pm 0.07$	$15.27 \pm 0.37$	$16.72 \pm 0.40$	$19.42 \pm 0.33$	$22.66 \pm 0.40$	$23.68 \pm 0.24$	$25.09 \pm 0.61$		
(f) t-Butyl chloride: chlorocyclohexane (reaction time 300 s)									
Temp. (°C)	154	121	105	96	72	58	32		
$[Me_3CH] / [cyclo-C_6H_{12}]$	$4.03 \pm 0.32$	$4.56 \pm 0.01$	$5.52 \pm 1.14$	$5.77 \pm 0.03$	$2.66 \pm 0.08$	$3.18 \pm 0.01$	$3.19 \pm 0.05$		
(g) 2-Chloro-2-methylbutane: chlorocyclohexane (reaction time 600 s)									
Temp. (°C)	147	123	105	92	75	71	62	60	
$[C_2H_5] / [cyclo-C_6H_{12}]$	$4.24 \pm 0.09$	$4.77 \pm 0.10$	$3.08 \pm 0.08$	$2.63 \pm 0.10$	$2.03 \pm 0.15$	$2.87 \pm 0.06$	$2.12 \pm 0.06$	$2.17 \pm 0.04$	
Temp. (°C)	55	40	40	39	32				
$[C_4H_9] / [cyclo-C_6H_{12}]$	$1.91 \pm 0.10$	$2.49 \pm 0.10$	$2.33 \pm 0.10$	$2.79 \pm 0.16$	$2.45 \pm 0.11$				
(h) 1,3-Dichloro-3-methylbutane: chlorocyclohexane (reaction time 600 s)									
Temp. (°C)	145	115	89	73	68	55			
$[1-Cl, 3-MeC_4H_9] / [cyclo-C_6H_{12}]$	$4.09 \pm 0.22$	$5.53 \pm 0.24$	$5.52 \pm 0.64$	$11.91 \pm 0.92$	$8.26 \pm 0.96$	$13.12 \pm 0.01$			
(i) 1-Chloro-4-fluorobutane (reaction time 900 s)									
Temp. (°C)	184	161	100	83	73	65	39		
$[C_4H_9F] / [C_4H_9Cl]$	$11.41 \pm 1.15$	$14.07 \pm 0.47$	$23.55 \pm 1.58$	$26.14 \pm 2.28$	$30.95 \pm 2.10$	$25.25 \pm 0.53$	$57.06 \pm 1.93$		
(j) 1-Bromo-4-chlorobutane (reaction time 3600 s)									
Temp. (°C)	125	97	84	70	50				
$[C_4H_9Cl] / [C_4H_9Br]$	$19.98 \pm 0.91$	$13.28 \pm 0.61$	$14.26 \pm 1.88$	$12.71 \pm 1.04$	$10.78 \pm 0.71$				
The unexpected temperature coefficient indicates that the system was over reacted and some butyl bromide was further reduced to butane.									
(k) 2,2-Dichloropropane: fluorocyclohexane (reaction time 300 s)									
Temp. (°C)	150	128	104	70	51	41			
$[cyclo-C_6H_{12}] / [C_3H_7Cl]$	$1.20 \pm 0.02$	$1.67 \pm 0.06$	$1.96 \pm 0.02$	$3.74 \pm 0.01$	$4.19 \pm 0.07$	$4.87 \pm 0.01$			
(l) 2,2-Dichloropropane: chlorocyclohexane (reaction time 300 s)									
Temp. (°C)	154	129	96	82	68	43			
$[cyclo-C_6H_{12}] / [C_3H_7Cl]$	$1.51 \pm 0.01$	$1.93 \pm 0.01$	$2.77 \pm 0.02$	$3.61 \pm 0.01$	$4.70 \pm 0.08$	$6.21 \pm 0.08$			
(m) Carbon tetrachloride: bromocyclohexane (reaction time 90 s)									
Temp. (°C)	131	125	105	103	75	61	50	50	47
$[CHCl_3] / [cyclo-C_6H_{12}]$	$0.69 \pm 0.01$	$0.80 \pm 0.01$	$0.91 \pm 0.05$	$0.93 \pm 0.01$	$1.01 \pm 0.03$	$1.66 \pm 0.01$	$1.92 \pm 0.01$	$1.98 \pm 0.02$	$2.18 \pm 0.02$
(n) Carbon tetrachloride: chlorocyclohexane (reaction time 600 s)									
Temp. (°C)	156	137	100	66	45	35			
$[CHCl_3] / [cyclo-C_6H_{12}]$	$9.32 \pm 0.14$	$11.40 \pm 0.61$	$13.46 \pm 0.14$	$22.36 \pm 0.59$	$24.25 \pm 1.30$	$24.88 \pm 3.17$			
(o) Chloroform: 1,1,1-trichloroethane (reaction time 300 s)									
Temp. (°C)	157	132	102	73	67	39	38		
$[C_2H_5Cl_3] / [CH_2Cl_2]$	$1.34 \pm 0.09$	$1.45 \pm 0.04$	$1.42 \pm 0.07$	$1.65 \pm 0.08$	$1.59 \pm 0.03$	$1.78 \pm 0.04$	$1.90 \pm 0.11$		
(p) Chloroform: 1,1,1,2-tetrachloroethane (reaction time 600 s)									
Temp. (°C)	150	129	112	79	61	45	31		
$[CHCl_2CH_2Cl] / [CH_2Cl_2]$	$1.49 \pm 0.01$	$1.50 \pm 0.03$	$1.51 \pm 0.01$	$2.35 \pm 0.02$	$2.44 \pm 0.01$	$2.89 \pm 0.05$	$2.73 \pm 0.01$		
$[CH_2Cl_2] / [CH_2CCl_3]$	$32.39 \pm 0.01$	$31.36 \pm 0.01$	$24.96 \pm 0.01$	$17.83 \pm 0.07$	$16.62 \pm 0.06$	$13.68 \pm 0.09$	$13.19 \pm 0.04$		
(q) Chloroform: 1,1,1-trichlorotrifluoroethane (reaction time 600 s)									
Temp. (°C)	155	144	132	105	80	61	50	43	
$[C_2HCl_3F_3] / [CH_2Cl_2]$	$4.90 \pm 0.10$	$4.25 \pm 0.02$	$3.68 \pm 0.03$	$3.78 \pm 0.02$	$3.24 \pm 0.01$	$3.26 \pm 0.02$	$3.25 \pm 0.01$	$3.22 \pm 0.01$	
(r) Chloroform: 1,1,1,3-tetrachloropropane (reaction time 600 s)									
Temp. (°C)	156	128	105	94	92	72	67	64	
$[CH_2Cl_2] / [C_3H_5CCl_3]$	$6.37 \pm 0.09$	$4.47 \pm 0.01$	$2.58 \pm 0.01$	$3.73 \pm 0.01$	$3.56 \pm 0.01$	$3.54 \pm 0.01$	$2.47 \pm 0.01$	$2.95 \pm 0.01$	
$[Cl(CH_2)_3Cl] / [CH_2Cl_2]$	$1.61 \pm 0.01$	$3.52 \pm 0.01$	$4.01 \pm 0.01$	$3.28 \pm 0.01$	$4.20 \pm 0.02$	$4.31 \pm 0.02$	$4.09 \pm 0.09$	$3.97 \pm 0.01$	
$[CH_2Cl_2] / [C_3H_5CCl_3]$	$2.59 \pm 0.01$	$3.14 \pm 0.01$	$2.66 \pm 0.01$						
$[Cl(CH_2)_3Cl] / [CH_2Cl_2]$	$5.29 \pm 0.01$	$4.31 \pm 0.02$	$4.20 \pm 0.02$						

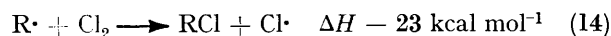
TABLE 1 (Continued)

(s) 1,1,1-Trichloroethane: pentachloroethane (reaction time 300 s)							
Temp. (°C)	159	129	108	86	68	42	31
$[\text{CH}_2\text{ClCCl}_3] / [\text{CH}_2\text{CICH}_3]$	$6.62 \pm 0.38$	$7.51 \pm 0.46$	$8.51 \pm 1.34$	$9.87 \pm 0.35$	$11.78 \pm 0.84$	$11.81 \pm 0.87$	$11.91 \pm 0.44$
$[\text{CHCl}_2\text{CHCl}_2] / [\text{CH}_2\text{CHCl}_2]$	$2.48 \pm 0.33$	$2.85 \pm 0.23$	$3.13 \pm 0.46$	$3.85 \pm 0.11$	$4.86 \pm 0.39$	$4.62 \pm 0.07$	$5.06 \pm 0.12$
(t) 1,1,1-Trichloroethane: trichlorofluoromethane (reaction time 300 s)							
Temp. (°C)	132	114	93	66	36		
$[\text{C}_2\text{H}_4\text{Cl}_2] / [\text{CHCl}_2\text{F}]$	$1.03 \pm 0.04$	$0.77 \pm 0.08$	$1.06 \pm 0.01$	$2.31 \pm 0.09$	$1.31 \pm 0.13$		
(u) Carbon tetrachloride: dichloromethane (reaction time 300 s)							
Temp. (°C)	150 $\pm$ 2	119	82	70			
$[\text{CHCl}_3] / [\text{CH}_2\text{Cl}_2]$	$3.77 \pm 0.91$	$2.01 \pm 0.16$	$2.01 \pm 0.10$	$2.36 \pm 0.15$			
(v) Chloroform: chlorocyclohexane (reaction time 600 s)							
Temp. (°C)	163	144	110	79	63	50	
$[\text{CH}_2\text{Cl}_2] / [\text{cyclo-C}_6\text{H}_{11}]$	$3.12 \pm 0.19$	$3.34 \pm 0.07$	$4.15 \pm 0.21$	$6.52 \pm 0.47$	$6.72 \pm 0.33$	$10.92 \pm 0.55$	
(w) Carbon tetrachloride: chlorocyclohexane (reaction time 600 s)							
Temp. (°C)	156	137	100	66	45	35	
$[\text{CHCl}_3] / [\text{cyclo-C}_6\text{H}_{11}]$	$9.32 \pm 0.14$	$11.40 \pm 0.61$	$13.46 \pm 0.14$	$22.36 \pm 0.59$	$24.25 \pm 1.30$	$24.88 \pm 3.17$	

hydrogen abstraction by chlorine atoms. The overall



reaction is thus exothermic ( $\Delta H$  ca.  $-47$  kcal mol $^{-1}$ ) compared with chlorination which is less exothermic ( $\Delta H$  ca.  $-27$  kcal mol $^{-1}$ ).



Chlorine abstraction by trialkyltin radicals is thus slightly more exothermic than hydrogen abstraction by chlorine atoms. We would thus expect chlorine abstraction to exhibit similar selectivity to that observed in photo-chlorination. Bromine abstraction by trialkyltin radicals is more exothermic ( $\Delta H - 12$  kcal mol $^{-1}$ ) and would therefore be expected to be more facile than chlorine abstraction. Data are not available on the strength of trialkyltin fluoride bonds though the great strength of carbon-fluorine bonds in alkyl fluorides suggests that abstraction of fluorine by trimethyltin radicals is likely to be difficult. In making these predictions it must be borne in mind that thermochemical data relating to organotin compounds are far less certain than for hydrocarbons and alkyl halides. Nevertheless the above figures are consistent with the occurrence of very long chains in these halogen abstraction reactions and lead us to expect little selectivity. The relative rates of chlorine abstraction are shown in Table 2. The data in Table 2 were obtained from the results in Table 1, interpolated where necessary.

Table 3 compares the selectivity observed in the present study with the selectivity observed in gas-phase chlorination under similar conditions.<sup>18</sup>

The close similarity between the selectivity of the two processes is consistent with the approximate thermochemical data discussed above. The results also confirm that the selectivity observed in chlorination

(tertiary > secondary > primary) can be principally attributed to changes in the strength of the hydrogen bond broken, rather than in polar effects, as has been suggested.<sup>19</sup> If polar effects due to alkyl substituents were important we would observe a reversal of selectivity in halogen abstraction. Since the activation

TABLE 2

Relative rates of chlorine abstraction from chloroalkanes taking chlorocyclohexane as standard (100 °C)

R-Cl	Relative rate
Primary	
$\text{Cl}[\text{CH}_2]_4\text{Cl}$	$0.51 \pm 0.03$
$\text{Me}_2\text{CClCH}_2\text{CH}_2\text{Cl}$	$0.36 \pm 0.09$
$\text{Me}_2\text{CHCH}_2\text{CH}_2\text{Cl}$	$0.34 \pm 0.03$
$\text{Me}_3[\text{CH}_2]_6\text{Cl}$	$0.73 \pm 0.09$
Secondary	
$\text{cyclo-C}_6\text{H}_{11}\text{Cl}$	1.00
$\text{Cl}[\text{CH}_2]_2\text{CHMeCl}$	$1.28 \pm 0.03$
Tertiary	
$\text{Me}_3\text{CCl}$	$3.90 \pm 0.50$
$\text{C}_2\text{H}_5\text{CMe}_2\text{Cl}$	$3.16 \pm 0.21$
$\text{Cl}[\text{CH}_2]_2\text{CMe}_2\text{Cl}$	$6.30 \pm 0.30$

TABLE 3

Comparison of chlorine abstraction by trimethyltin radical with hydrogen atom abstraction by chlorine atoms. Relative selectivities  $\text{RS}^{\sigma_1}$  at 100° (average values)

Chlorine abstraction by $(\text{Me})_3\text{Sn}\cdot$	$\text{RS}^{\sigma_1}$	Hydrogen abstraction by $\text{Cl}\cdot$	$\text{RS}^{\sigma_1}$
$\text{RCH}_2\text{-Cl}$	1	$\text{RCH}_2\text{-H}$	1
$\text{R}_2\text{CH-Cl}$	2.4	$\text{R}_2\text{CH-H}$	4
$\text{R}_3\text{C-Cl}$	9.2	$\text{R}_3\text{C-H}$	5

energy for chlorine atom abstraction from any site is unlikely to be  $>2$  or  $3$  kcal mol $^{-1}$ , the activation energy differences between various sites must be of the order of 1 kcal mol $^{-1}$  or less. The chlorine abstractions were all studied over a range of temperatures and Table 1 confirms that the activation energy differences are indeed very small, often  $<1$  kcal mol $^{-1}$ . The Arrhenius parameters are not tabulated because using the present techniques the results are too scattered for such small differences to be estimated accurately.

Reference was made in the introduction to the work of Szwarc<sup>12</sup> and that of Whittle.<sup>10</sup> These authors found hydrogen abstraction greatly favoured when

<sup>19</sup> A. B. Ash and H. C. Brown, *Rec. Chem. Progr.*, 1948, **9**, 81.

simple thermochemistry would predict halogen abstraction to be at least as facile. With trimethyltin radicals the thermochemistry is much more in favour of halogen abstraction. Deuteriochloroform reacted with trimethyltin hydride to give  $\text{CHDCl}_2$ , but no  $\text{Me}_3\text{SnD}$  could be detected. Similarly when trimethyltin deuteride was photolysed in the presence of cyclohexane no deuterium was incorporated into the cyclohexane. Thus within the limits of the experimental techniques employed no hydrogen abstraction by trimethyltin radicals could be detected.

TABLE 4

Relative rates of halogen abstraction by trimethyltin radicals (chlorine as standard) at 100 °C

Primary	
$\text{Cl}[\text{CH}_2]_4\text{F}$	$0.04 \pm 0.0$
$\text{Cl}[\text{CH}_2]_4\text{Cl}$	1.00
$\text{Cl}[\text{CH}_2]_4\text{Br}$	14 (Over-reacted)
Secondary	
cyclo- $\text{C}_6\text{H}_{11}\text{F}$	$0.80 \pm 0.02$
cyclo- $\text{C}_6\text{H}_{11}\text{Cl}$	1.00
cyclo- $\text{C}_6\text{H}_{11}\text{Br}$	$16.25 \pm 0.92$

The relative rates of abstraction of the halogens by trimethyltin radicals are shown in Table 4. The fluorine figure is difficult to estimate because the extent of abstraction is so small, while the bromine figure is in some doubt because over-reaction was necessary to obtain sufficient chlorine abstraction to measure. The relative rates are in accord with expectation. The reactions are all exothermic and hence the strength of the bond broken (the carbon-halogen bond) has a greater influence than the strength of the bond formed (the tin-halogen bond), on the relative rates.

In order to investigate possible polar effects chlorine abstraction from polyhalogenoalkanes was investigated. Simple dihalogenoalkanes presented considerable problems, both experimental and in the interpretation of the results. It was therefore decided to examine chlorine abstraction from trichloromethyl groups  $\text{CCl}_3\text{-X}$ , where X was either a single atom or a carbon atom carrying further substituents. In the latter case the attacked halogen was three atoms away from the polar substituent; the results are shown in Table 5.

The increase in reactivity in going from chloroform to carbon tetrachloride is expected. The carbon-chlorine bonds are almost certainly weaker in the latter compound and Alcock and Whittle<sup>10</sup> found the same order of chlorine abstraction by trifluoromethyl radicals. On the other hand the increased reactivity of fluorotrichloromethane cannot be explained in these terms. Tomkinson and Pritchard found that methyl

radicals abstract chlorine at approximately one tenth the rate from fluorotrichloromethane than from carbon tetrachloride.<sup>8</sup> The fact that fluorotrichloromethane

TABLE 5

Chlorine abstraction from trichloromethyl derivatives by trimethyltin radicals at 100°

(a) Substituted trichloromethanes (chloroform as standard)	
$\text{XCCl}_3$	Relative rate
$\text{HCCl}_3$	1.00
$\text{ClCCl}_3$	$2.78 \pm 0.1$
$\text{FCCl}_3$	1.5
(b) Substituted 1,1,1-trichloroalkanes ( $\text{CH}_3\text{CCl}_3$ as standard)	
$\text{RCCl}_3$	Relative rate
$\text{H}_3\text{CCCl}_3$	1.00
$\text{ClH}_2\text{CCCl}_3$	$1.37 \pm 0.1$
$\text{Cl}_2\text{HCCCl}_3$	$3.10 \pm 0.2$
$\text{F}_3\text{CCCl}_3$	$2.47 \pm 0.2$

is more reactive in the present work provides evidence for the 'reverse' polar effect discussed at the beginning of this paper.

The trichloroethane derivatives provide more striking evidence of the 'reverse' polar effect. It is most unlikely that the additional chlorine atom in 1,1,1,2-tetrachloroethane can have an appreciable effect on the carbon-chlorine bonds of the trichloromethyl group. Hence the increased reactivity of the  $\text{CCl}_3$  group can be attributed to the polar effect, which becomes stronger in pentachloroethane resulting in even more enhanced reactivity.

The trifluoromethyl group would be expected to increase the carbon-chlorine bond strengths (hydrogen abstraction from  $\text{CF}_3\text{CH}_3$  is very difficult<sup>20</sup>). In fact Quick and Whittle have studied chlorine abstraction by trifluoromethyl radicals from 1,1,1-trichloroethane and -trifluoroethane and observe a reactivity  $\text{CH}_3\text{CCl}_3 > \text{CF}_3\text{CCl}_3$  [ca. 3 : 1 at 100°; the activation energy for the former compound is very much lower but this is to some extent offset by a larger pre-exponential factor  $k_{\text{CH}_3\text{CCl}_3} = 3 \times 10^{11} \exp(-9,700/2.3RT)$ ;  $k_{\text{CF}_3\text{CCl}_3} = 9 \times 10^{12} \exp(-12,700/2.3RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ].<sup>21</sup> The reactivity observed for chlorine abstraction by trimethyltin radicals in the present work provides strong evidence for the predicted 'reverse' polar effect. Trimethyltin radicals are very unselective and the transition state will resemble the reactants rather than the products. The extent of the polar effect will therefore be small, but it is nonetheless clearly manifest.

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<sup>20</sup> J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, 1966, **62**, 1553.

<sup>21</sup> L. M. Quick and E. Whittle, *J.C.S. Faraday I*, 1972, 878.