660. *The Chlorination of Some n-Alkanes and Alkyl Chlorides*

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The liquid-phase chlorination of n-hexane, n-octane, 1-, 2-, and 3-chlorohexane, and 1-chloro-octane, using elemental chlorine, has been studied at 20°. Product yields of the mono and higher chlorides, together with unreacted n-hexane, have been compared with a statistical model for the chlorination of alkanes. The overall reactivities of the individual reactants have been measured, relative to n-hexane, and are in the order: n-octane > n-hexane = 1-chloro-octane > 1-chlorohexane > 2-chlorohexane > 3-chlorohexane. Yields of the monochlorides from the n-alkanes and dichlorides from the monochloroalkanes, respectively, have been determined by means of gas-chromatographic analysis. Relative selectivities for the abstraction of hydrogen by atomic chlorine have been calculated. In addition, the yields of the diastereoisomeric forms of 2,3-, 2,4-, and 2,5-dichlorohexane derived from 2-chlorohexane have been measured, and the steric course of the chlorination reaction is discussed.

The chlorination of aliphatic hydrocarbons and their derivatives has been the subject of several reviews.[1] Of the chloro-alkanes investigated, those containing less than five carbon atoms have been studied in greatest detail. The chlorination of some higher alkyl chlorides has been reported by Horner and Schläfer.[2] We have extended these studies by investigating the liquid-phase chlorination, at 20°, of the chloro-alkanes 1-, 2-, and 3-chlorohexane and 1-chloro-octane, and, in addition, the two alkanes n-hexane and n-octane. The purpose of our work was to compare the product yields for an n-alkane with those predicted from a statistical model, and to study the reactivities of the chloro-alkanes, directive effects, and the steric course of the chlorination reaction.

Experimental

Materials.—Chlorine. I.C.I. cylinder chlorine, containing, in the initial fraction, 5—10% (v/v) oxygen, was deoxygenated before use by " bleeding off " the initial 10% (by weight) of the cylinder contents. This procedure reduced the oxygen concentration to 15—50 p.p.m.

Alkanes. n-Hexane and n-octane were supplied by L. Light & Co. The two hydrocarbons were shown by gas-chromatographic analysis to contain less than 1% (w/w) of aromatic and aliphatic hydrocarbons as impurities, and were used without further purification.

Chloro-alkanes. Eastman-grade 1-chlorohexane and 1-chloro-octane were obtained from Kodak Ltd. 2-Chlorohexane was prepared by the hydrochlorination of hex-1-ene. 3-Chlorohexane was prepared by reaction of hexan-3-ol with thionyl chloride. These materials contained trace impurities in the form of isomers and homologues of the corresponding chloro-alkanes. Chlorination did not result in the formation of any anomalous products.

Apparatus and Procedure.—The alkane was weighed into the reaction vessel, consisting of a round-bottom flask with a thermometer pocket, gas inlet and outlet, and a vane-disc stirrer capable of 2000 r.p.m. The apparatus was maintained at 20° ± 1° by immersion in a thermostat. The reactant gas (chlorine) and " white spot " nitrogen (<10 p.p.m. oxygen), used for degassing purposes, were dried with concentrated sulphuric acid and metered into the reaction vessel by means of rotameters. The gas inlet was positioned directly below the stirrer for efficient mixing of the gas and alkane. The exit gases left the flask *via* a water-jacketed condenser and a solid carbon dioxide–trichloroethylene cold-finger such that any alkane carried over in the gas stream was returned to the reaction vessel. The product gas (hydrogen chloride) and any excess of chlorine were then absorbed in water and sodium hydroxide solution, respectively.

In each run, nitrogen (40 l./hr.) was passed through the whole apparatus, including the reactant liquid, for 1 hr., to remove the oxygen present. The chlorine was then bubbled into

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[1] For example, see (*a*) J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336; (*b*) G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens, and G. Verbeke, *Chem. Rev.*, 1963, **63**, 355.

[2] L. Horner and L. Schläfer, *Annalen*, 1960, **635**, 31.

the alkane at the required flow-rate, with the nitrogen turned off. Reaction occurred almost immediately, and hydrogen chloride was evolved. When the desired extent of chlorination had been reached, the chlorine was turned off and the reactant again flushed with nitrogen to remove any dissolved chlorine and hydrogen chloride. The extent of the reaction was determined by titration of the total hydrogen chloride evolved. Chlorinated products were analysed by means of gas chromatography.

Analysis.—Perkin-Elmer 452 and F11 instruments, fitted with flame-ionisation detectors, were used for the gas-chromatographic analysis. The columns contained stationary phases of polyethylene glycol (Carbowax) and sulpholane as follows. (i) 2 m.; 4 mm. dia.; Carbowax 1000, 10% (w/w) on M & B Embacel, 60—100 mesh; 10 p.s.i. nitrogen carrier-gas. (ii) 2 m.; 4 mm. dia.; Carbowax 20,000, 10% (w/w) on M & B Embacel, 60—100 mesh; 10 p.s.i. nitrogen carrier-gas. (iii) 4 m.; 6 mm. dia.; sulpholane, 15% (w/w) on M & B Embacel, 60—100 mesh; 8 p.s.i. nitrogen carrier-gas. Hydrogen and air supplies to the detector were 15 and 30 p.s.i., respectively.

The preparative instrument was an Aerograph Autoprep A-700, fitted with a thermal-conductivity detector and an automatic sample injector and collector. Preparative columns of diameter 1 cm. were made up in a similar manner to those used for analytical purposes. Helium, at *ca.* 200 ml./min., was the carrier gas.

Tables 1 and 2 give the retention times, relative to that of 2,2,4-trimethylpentane,[3] for the reactants and products on the analytical columns.

TABLE 1

Relative retention times for the alkanes and monochloroalkanes

			Monochloride (rel. retn. time)				
Reactant	Column	Temp.	Reactant	1-	2-	3-	4-
Hexane	(i)	60°	0·8	7·7	4·8	4·8	—
	(iii)	50	0·8	11·7	7·6	7·2	—
Octane	(ii)	70	1·9	30·0	18·2	16·9	15·3

TABLE 2

Relative retention times for the monochloro- and dichloro-alkanes on column (ii)

		Dichloride (rel. retn. time)														
Reactant	Temp.	Reac-tant	1,1-	1,2-	1,3-	1,4-	1,5-	1,6-	1,7-	1,8-	2,2-	2,3-	2,4-	2,5-	3,3-	3,4-
1-Cl·C_6H_{13}	130°	2·1	4·2	5·7	6·8	9·4	11·0	15·9								
2-Cl·C_6H_{13}	130	1·7		5·7			11·0				2·9	4·2 4·7	4·4 5·0	6·4 6·8		
3-Cl·C_6H_{13}	130	1·7			6·8	9·4						4·2 4·7	4·4 5·0		3·0	4·0 4·4
1-Cl·C_8H_{17}	150	3·5	6·8	9·1	10·4	12·8	14·5	15·9	17·3	23·9						
B. p. of $Cl_2C_6H_{12}$			162°	174	181	193	199·5	214			148	162 166·5	164 169	179 181		160 164

The dichlorides from the 1-chloro-alkanes were identified by means of nuclear magnetic resonance analysis of samples obtained by preparative chromatography. Their separation on " boiling point " columns is facilitated by the regular increase in boiling point of the dichlorides with increasing separation of the two chlorine atoms on the carbon chain. The products from the chlorination of 2- and 3-chlorohexane are not readily separated on preparative columns of low efficiency. Identification, in the latter cases, was effected by comparison with model compounds. 2,5-, 2,3-, and 3,4-Dichlorohexane were prepared by chlorination of hexane-2,5-diol, hex-2-ene, and hex-3-ene, respectively. 2,4-Dichlorohexane was identified by " cross-checking " the products from 2- and 3-chlorohexane, since both reactants give the 2,4-isomer on chlorination.

The boiling points of seven of the dichlorohexanes, namely, 1,2-, 1,5-, 1,6-, 2,2-, 2,3-, 2,5-, and 3,4-dichlorohexane, are reported in the literature.[4] A graph of $\log_{10}$(retention time) against boiling point for 1,2-, 1,6-, and 2,2-dichlorohexane, was a straight line from which the

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[3] Recommendations on Nomenclature and Presentation of Data in Gas Chromatography, Third Symposium on Gas Chromatography, Edinburgh, June 1960.

[4] E. H. Huntress, " Organic Chlorine Compounds," Wiley, New York, 1948.

boiling points of the remaining isomers were determined. The values are given in the bottom line of Table 2.

Product yields were calculated from peak areas or calibrated peak heights. The response of the flame-ionisation detector to the isomeric mono- or di-chlorohexanes and chloro-octanes was determined for a range of detector currents from 10^{-11} to 10^{-9} A. All samples were analysed within this sensitivity range. The following were typical of the calibration tests applied: (i) Solutions containing 1,6-dichlorohexane in n-hexane gave a straight line plot for either peak area or peak height against concentration of 1,6-dichlorohexane; (ii) A mixture of dichlorohexanes, obtained by the chlorination of 1-chlorohexane, was progressively diluted with n-hexane, and the ratio of the peak area relative to 1,6-dichlorohexane was determined for each isomer. The standard deviation for each isomer ratio as a function of concentration ranged from ± 2 to $\pm 11\%$. The deviation of the ratios for the different isomers at each concentration was similar; (iii) Identical mixtures of dichlorohexanes, similar to those used in (ii), were analysed by using both a flame-ionisation detector and a thermal-conductivity detector. The ratios of the individual peak areas, relative to that of the 1,6-isomer, were the same within the errors quoted. Such investigations illustrate that, for our analytical conditions, the flame-ionisation detector gives a similar response for equal weights of the isomeric chlorohexanes, which is not concentration-dependent. This was also found to be the case for the isomeric chloro-octanes.

RESULTS AND DISCUSSION

n-Hexane: *Composition of Reactant After Chlorination.*—In Figure 1, yields of mono and higher chlorides, together with unreacted hexane, are represented as a function of the number of moles of chlorine reacted per mole of the original alkane. The results indicate that the starting material is not completely consumed until $\gg$1 mole of chlorine has reacted per mole of alkane, and that the monochloride yield passes through a maximum corresponding to 1 mole of chlorine reacted. The composition of the reactant at this

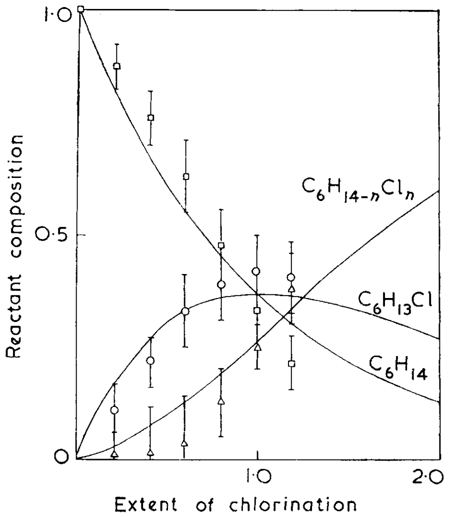

FIGURE 1. The composition of the reactant (mole fraction of total) as a function of the extent of chlorination (the number of moles of chlorine reacted per mole of original hexane). Comparison of experiment with theory. Solid lines are theoretical yields. Points are experimental yields: □ n-hexane; ○ monochlorohexane; △ polychlorohexanes

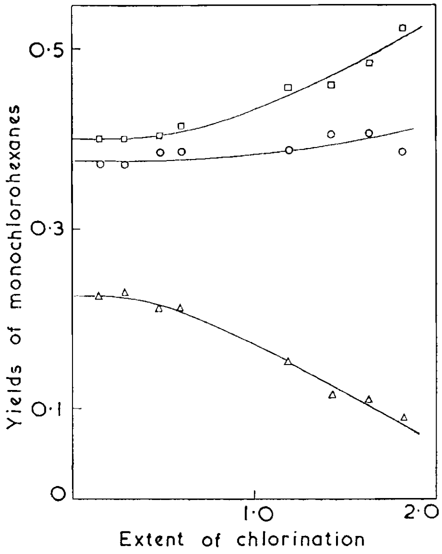

FIGURE 2. Dependance of the yields of the monochlorohexanes (represented as a fraction of the total monochloride) on the extent of chlorination (the number of moles of chlorine reacted per mole of original hexane). □ 3-chlorohexane; ○ 2-chlorohexane; △ 1-chlorohexane

point, on a mole/mole basis, is n-hexane 33%, monochloride 42%, and higher chlorides 25%. This behaviour is in accordance with the prediction of Asinger;[5] similarly, the yields of the di-, tri-, tetra-chlorides, etc., should pass through maxima when 2, 3, 4, etc., moles of chlorine have reacted.

Figure 1 also compares our results with the yields expected on the basis of a statistical theory of chlorination due to Schuhler,[6] who treats a series of consecutive reactions kinetically. Thus a chlorination series may be envisaged:

$$\begin{aligned}
C_6H_{14} + Cl &\xrightarrow{k_1} C_6H_{13} + HCl \\
C_6H_{13}Cl + Cl &\xrightarrow{k_2} C_6H_{12}Cl + HCl \\
C_6H_{12}Cl_2 + Cl &\xrightarrow{k_3} C_6H_{11}Cl_2 + HCl \\
&\vdots \\
C_6HCl_{13} + Cl &\xrightarrow{k_{14}} C_6Cl_{13} + HCl
\end{aligned}$$

The approximations made are as follows. (i) All the hydrogen atoms in the alkane possess the same reactivity towards abstraction by atomic chlorine, *i.e.*, no allowance is made for the greater rate of hydrogen abstraction from a CH_2 than from a CH_3 group. This is essentially correct for long-chain hydrocarbons. (ii) The presence of chlorine substituents in the alkane does not affect the rate of abstraction of hydrogen atoms. This will apply only at relatively low conversion of alkane to chloroalkane, and is inapplicable for high conversions (see later discussion). (iii) As a consequence of (i) and (ii), k_1, k_2, $k_3 \ldots k_{14}$ are proportional to the number of hydrogen atoms in each molecule.

The kinetics of such a reaction scheme lead to the following expression for the yields of the chlorinated hexanes,

$$\begin{aligned}
[C_6H_{14}] &= e^{-x} \\
[C_6H_{13}Cl] &= xe^{-x} \\
[C_6H_{14-n}Cl_n] &= \frac{x^n}{n!}e^{-x} \quad (n = 1 \ldots\ldots 13) \\
[C_6Cl_{14}] &= 1 - \left[1 + x + \frac{x^2}{2!} + \cdots\cdots \frac{x^{14-1}}{(14-1)!}\right]e^{-x},
\end{aligned}$$

where x is the number of moles of chlorine reacted per mole of hexane.

The agreement between the two sets of results (Figure 1) is within the experimental error. Although this comparison does not provide a test of Schuhler's approximation (ii) at high conversions, it does show that these assumptions are legitimate for n-hexane, provided that the conversion of alkane to chloro-alkane is relatively low.

Distribution and Reactivities of the Monochlorides.—The yields of the monochlorides obtained by chlorination of n-hexane and n-octane to low conversions, *i.e.*, <5%, are given in Table 3. The distributions of the 1-, 2-, and 3-chlorohexanes are represented in Figure 2 as a function of the number of moles of chlorine reacted per mole of original hexane. As the extent of chlorination increases, the monochloride fraction becomes significantly enriched in 3-chlorohexane. The fraction of 2-chlorohexane remains approximately constant, while that of 1-chlorohexane decreases. Consequently, the

TABLE 3

Yields of monochlorides at 20°

Reactant	Monochloride (mole fraction)			
	1-	2-	3-	4-
n-Hexane	0·227	0·373	0·40	
n-Octane	0·186	0·267	0·274	0·271

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[5] F. Asinger, *Chemie*, 1944, **57**, 140.

[6] C. Schuhler, *Z. phys. Chem.* (*Leipzig*), 1962, **219**, 53.

reactivities of the three monochlorides towards further chlorination are in the order: 1-chlorohexane > 2-chlorohexane > 3-chlorohexane. These observations have been confirmed by competitive chlorination of the three monochlorides separately, in the presence of n-hexane. Experimentally, mixtures of alkane and monochloride, of known composition, were chlorinated to low conversion, and the yields of mono- and di-chlorides, respectively, determined for each reactant mixture. Table 4 summarises the results for hexane and octane derivatives.

TABLE 4

Relative reactivities measured at 20°

Reactants	Relative reactivities (mole/mole)	Reactants	Relative reactivities (mole/mole)
Hexane and 1-chlorohexane ...	1 : 0·55	Hexane and octane	1 : 1·35
Hexane and 2-chlorohexane ...	1 : 0·33	Hexane and 1-chloro-octane ...	1 : 1·00
Hexane and 3-chlorohexane ...	1 : 0·24	Octane and 1-chloro-octane ...	1 : 0·74

The relative reactivities of 1-, 2-, and 3-chlorohexane towards further chlorination are 1·0 : 0·60 : 0·43, respectively. The measurements are subject to a possible error of ±10%. As expected on the basis of an increased concentration of CH_2 groups in n-octane compared to n-hexane, the former is the more reactive of the two alkanes. Similarly, on account of a shorter chain-length, the presence of a terminal chlorine atom deactivates 1-chlorohexane to a greater extent than 1-chloro-octane.

Distribution of the Dichlorides.—The yields of the dichlorides obtained by the chlorination of 1-, 2-, and 3-chlorohexane and 1-chloro-octane are given in Table 5.

TABLE 5

Yields of dichlorides at 20°

Reactant	Dichloride (mole fraction)													
	1,1-	1,2-	1,3-	1,4-	1,5-	1,6-	1,7-	1,8-	2,2-	2,3-	2,4-	2,5-	3,3-	3,4-
1-Cl·C_6H_{13}	0·0214	0·111	0·116	0·293	0·280	0·127								
1-Cl·C_8H_{17}	0·0175	0·0528	0·115	0·184	0·176	0·177	0·169	0·110						
2-Cl·C_6H_{13}		0·0176			0·154				0·032	0·202	0·262	0·330		
3-Cl·C_6H_{13}			0·091	0·158						0·218	0·294*		0·07	0·17*

* The yields of the 3,4- and 2,4-dichlorohexanes from 3-chlorohexane are in doubt. The high-boiling stereoisomer of 3,4- cannot be separated from the low-boiling form of 2,4-; thus the yield of 2,4- is less than the value given, and the yield of 3,4-dichlorohexane correspondingly greater.

TABLE 6

Relative yields of stereoisomers

Reactant	Product dichlorohexane	Relative yields of stereoisomers	
		Low-b. p. isomer	High-b. p. isomer
2-Chlorohexane	2,3-	2·23	1·0
	2,4-	1·22	1·0
	2,5-	1·0	1·0
3-Chlorohexane	2,3-	2·8	1·0
	2,4-	—	—
	3,4-	—	—

The 2,3-, 2,4-, 2,5-, and 3,4-isomers each contain two asymmetric carbon atoms, and exist, therefore, as the *erythro*- and *threo*-forms. The relative yields of these two forms are summarised in Table 6. The identities of the low- and high-boiling-point isomers (see Table 2) can be ascertained by consideration of the structures of the intermediate radicals and the geometry of the transition state for the chlorination reaction.[7] For example, 2,3-dichlorohexane results from the intermediate radicals $CH_3{\cdot}CHCl{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ and $CH_3{\cdot}\dot{C}H{\cdot}CHCl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ from 2- and 3-chlorohexane, respectively. Interactions

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[7] P. S. Fredricks and J. M. Tedder, *Proc. Chem. Soc.*, 1959, 9.

between the groups adjacent to the unpaired electron favour a configuration in which the chlorine atom lies in the same plane as the hydrogen on the neighbouring carbon atom. For similar reasons, a " *trans* " approach of the chlorine to the substituent will predominate in the transition state. Such a mechanism will result in the formation of a greater yield of the *erythro*-component. As the distance between the substituent chlorine atom and the radical site increases, interaction between the incoming chlorine molecule and the substituent already present decreases until there is no preferential direction of approach.

Selectivity of the Hydrogen-abstraction Reaction.—The relative selectivity (RS_p^s) has been defined elsewhere.[1a] Results for n-hexane and n-octane, based on the yields in Table 3, are given in Table 7, and refer to the primary hydrogen atoms in the respective alkanes taken as unity. The selectivity values for the chloro-alkanes have been calculated from the relative reactivities and the yields reported in Tables 4 and 5, respectively.

TABLE 7

Relative selectivities for alkanes and monochlorides

	Carbon atom number (selectivities relative to primary hydrogen atoms in the alkane)							
Reactant	1-	2-	3-	4-	5-	6-	7-	8-
$n\text{-}C_6H_{14}$ ...	1·00	2·45 ± 0·13	2·60 ± 0·13	2·60 ± 0·13	2·45 ± 0·13	1·00		
$1\text{-}Cl{\cdot}C_6H_{13}$	0·16 ± 0·03	0·83 ± 0·08	1·24 ± 0·12	2·17 ± 0·11	2·10 ± 0·10	0·95 ± 0·05		
$2\text{-}Cl{\cdot}C_6H_{13}$	0·05 ± 0·01	0·29 ± 0·06	0·90 ± 0·09	1·16 ± 0·12	1·42 ± 0·14	0·68 ± 0·05		
$3\text{-}Cl{\cdot}C_6H_{13}$	0·18 ± 0·04	0·66*	0·42 ± 0·08	0·51*	0·90 ± 0·09	0·32 ± 0·06		
$n\text{-}C_8H_{18}$	1·00	2·15 ± 0·11	2·20 ± 0·11	2·20 ± 0·11	2·20 ± 0·11	2·20 ± 0·11	2·15 ± 0·11	1·00
$1\text{-}Cl{\cdot}C_8H_{17}$	0·21 ± 0·04	0·64 ± 0·12	1·4 ± 0·14	2·20 ± 0·11	2·10 ± 0·10	2·10 ± 0·10	2·03 ± 0·10	0·90 ± 0·10

* See footnote to Table 5.

RS_p^s for n-hexane, from our work, is 2·55 at 20° in the liquid phase. Chambers and Ubbelohde[8] have reported values of 3·03 and 2·30 at 88 and 238°, respectively, for the corresponding gas-phase reaction. It has been suggested[1a] that, in the liquid phase, a " cage effect " increases the relative reactivity of the primary positions.

The rates of chlorination of the secondary hydrogen atoms in n-octane are of the order of 0·85 times those for n-hexane (compared to the respective primary positions). The corresponding reactivity ratio[9] for n-hexane, compared to n-butane, is 0·86. Chambers and Ubbelohde[8] have attributed this decrease in reactivity with increasing chain length of the alkane to a steric effect caused by the ability of flexible molecules to assume " crumpled " configurations. This " crumpling " process will protect some of the secondary C–H bonds from reaction with chlorine, and will become more pronounced as the chain is lengthened. Alternatively, the decreased reactivity has been attributed to diminished stabilisation of the alkyl radical by hyperconjugation at the central carbon atoms as the chain length is increased.[9] This, however, would lead to the prediction that, in n-hexane, the selectivities should be lower at C-3 and C-4 than at C-2 and C-5; this is not the case (Table 7) for our reaction conditions.

The ratio of the overall reactivity of n-octane to that of n-hexane is 1·35 : 1 (Table 4), which, within the experimental error, is in agreement with the ratio of the sums of the relative selectivities for the individual molecules, *i.e.*, 1·23 : 1.

The presence of a chlorine substituent decreases the tendency for hydrogen abstraction to occur from sites in its vicinity. This has been attributed to the inductive effect, which decreases rapidly with increasing distance from the substituent. Fredricks and Tedder[9,10] have determined the values of RS_p^s for the chlorination of 1-chloro-butane and -pentane in the vapour phase at 78°. The rates of chlorination at C-3 in 1-chlorobutane and at the

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[8] G. Chambers and A. R. Ubbelohde, *J.*, 1955, 285.
[9] P. S. Fredricks and J. M. Tedder, *Chem. and Ind.*, 1959, 490.
[10] P. S. Fredricks and J. M. Tedder, *J.*, 1960, 144.

secondary hydrogen atoms in n-butane are similar. The greater reactivity of C-4 compared to C-3 in 1-chloropentane is assigned [9,10] to the greater possibility of hyperconjugation at C-4. The relative values of RS_p^s for 1-chloro-butane,[9,10] -pentane,[9] -hexane, and -octane are given in Table 8. It can be seen that, in the longer-chain compounds, the values for the secondary hydrogen atoms reach a maximum and are constant at C-4 and beyond. A similar trend is found by calculating the relative values of RS for 1-chlorohexane and -octane from the data of Horner and Schläfer,[2] obtained by chlorination at 80°. It may be concluded that a chlorine substituent at C-1 decreases the reactivity at C-1, C-2, and C-3. C-5 in 1-chlorohexane and C-7 in 1-chloro-octane do not exhibit the greater reactivity that would be expected if hyperconjugation were important. The range of the deactivation process suggests that factors in addition to the inductive effect of the chlorine substituent contribute to the low reactivity at C-3. The yields of the stereoisomeric forms of the 2,4-dichloride from 2-chlorohexane are not equal, indicating that the steric effect of the substituent is operative over three carbon atoms. The interaction is ineffective at a distance of four carbon atoms (Table 6). Reactivity values for 1-chloro-hexane and -octane are in agreement with this conclusion.

TABLE 8

Relative values of RS for 1-chloro-alkanes

	Carbon atom number (relative value of RS)							
Reactant	1-	2-	3-	4-	5-	6-	7-	8-
1-Chlorobutane	1	2·6	4·6	1·3	—	—	—	—
1-Chloropentane	1	2·5	4·7	6·9	1·3	—	—	—
1-Chlorohexane	1	5·2	7·7	13·6	13·1	5·9	—	—
1-Chloro-octane	1	3·1	6·7	10·5	10·0	10·0	9·7	4·3

The reactivities of the hydrogen atoms at C-1 for 1-chlorohexane and 1-chloro-octane are 0·17 and 0·23, respectively, compared to *ca.* 1·0 at the terminal positions. These values are much less than that of 0·8 for n-butyl chloride in the vapour phase at 78°,[10] but are close to those of 0·3 and 0·4 for n-hexyl chloride and n-octyl chloride, respectively, at 80°.[2]

The relative selectivities for the secondary alkyl chlorides (Table 7) show that every position in these two molecules is deactivated by the chlorine substituent, although this would not be expected from the reactivities of the 1-chloro-alkanes. For example, the predicted behaviour would suggest that C-5 and C-6 in 2-chlorohexane and C-6 in 3-chlorohexane should have reactivities similar to those of the corresponding positions in n-hexane. This effect cannot be attributed to steric interactions, or to an inductive mechanism on account of its long range. The hydrogen atoms on C-1 in 2-chlorohexane, C-2 in 1-chlorohexane, and C-3 in 2-chlorohexane possess reactivities, relative to the corresponding positions in n-hexane, of *ca.* 0·05, 0·33, and 0·50, respectively. As these positions are equidistant from the substituent chlorine atom, the inductive and steric effects are similar for each position, but the extent of deactivation is different. The same general tendency has been recorded for the chlorobutanes,[11] and has been assigned to a change in hyperconjugation at each position. However, for the chlorohexanes, the probability of radical stabilisation by hyperconjugation at these positions is small, and no explanation in these terms suggests itself for the effect observed.

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[11] P. S. Fredricks and J. M. Tedder, *J.*, 1961, 3520.