The Effect of Molecular Structure of Paraffins on Relative Chlorination Rates.
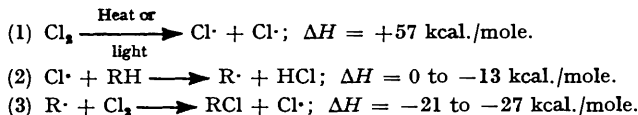
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Comparisons between homologues and isomers show that within the reaction range investigated the overall rate of monochlorination increases with increasing chain length and decreases with chain branching. This influence of molecular structure on monochlorination is analogous to its influence on rates of oxidation.

Relative reaction rates of chlorine atoms with primary, secondary, and tertiary hydrogen atoms in paraffins are discussed in the light of previous publications and of new experimental findings. For normal paraffins, the reactivity of secondary relative to primary hydrogen appears to decrease as the chain lengthens. An important factor may be the flexibility of the paraffins and their relative ability to assume crumpled forms.

A change observed in the surface activity of Pyrex glass during chlorination is interpreted as due to the replacement of hydrophilic groups in the surface by hydrophobic organosilicon groups.

In the physical chemistry of paraffins, a key problem is to interpret the marked influence of molecular structure on reactivity, notwithstanding the presence of much the same C–H and C–C bonds in all cases. This influence of molecular structure is particularly marked in oxidation, which may, however, involve some rather special reaction steps (Small and Ubbelohde, *J. Appl. Chem.*, 1953, **3**, 193). Reactions of the paraffins which involve simpler steps can be of value in elucidating the controlling factors. For this reason, chlorination in the gas phase has been re-investigated.

The thermal and photochemical chlorination of paraffins is believed to proceed by a chain mechanism (Pease and Walz, *J. Amer. Chem. Soc.*, 1931, **53**, 3728; Yuster and Reyerson, *J. Phys. Chem.*, 1935, **39**, 859; Vaughan and Rust, *J. Org. Chem.*, 1940, **5**, 449) involving the steps :

(1) $Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} Cl\cdot + Cl\cdot$; $\Delta H = +57$ kcal./mole.

(2) $Cl\cdot + RH \longrightarrow R\cdot + HCl$; $\Delta H = 0$ to -13 kcal./mole.

(3) $R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$; $\Delta H = -21$ to -27 kcal./mole.

The approximate heats of reaction indicated above are based on $D(Cl–Cl) = 57\cdot1$ kcal., $D(H–Cl) = 102\cdot1$ kcal., and the values of $D(R–H)$ and $D(R–Cl)$ quoted by Lane, Linnett, and Oswin (*Proc. Roy. Soc.*, 1953, A, **216**, 361). Since stage (2) is probably rate-determining, the effect of molecular structure on relative rates of chlorination is likely to depend mainly on local bond energies and on steric factors.

In the present work, the reactivities of a number of isomeric and homologous C_5–C_8 paraffins towards chlorine have been compared. The results show that the order of reactivity is similar to that found in oxidation, although the effects of molecular structure are much less pronounced.

It has been suggested (Ubbelohde and McCoubrey, *Discuss. Faraday Soc.*, 1951, **10**, 94) that the ability of flexible molecules to assume crumpled configurations may be important for hydrocarbon reactivity. Further evidence of this has now been obtained by analysis of the monochlorination products of *n*-hexane; the reactivity of the secondary relative to the primary hydrogen atoms appears to be appreciably less than has been reported (Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1936, **28**, 333) for chlorination of the lower paraffins.

EXPERIMENTAL

Purification of Materials.—Cylinder nitrogen was freed from oxygen by passage through a large steel tube containing copper turnings at 550°. Subsequently, moisture was removed

in a " Birlec Lectro Dryer." The surface of the copper in the deoxygenator was kept in an active condition by frequent regeneration with hydrogen.

Commercial chlorine was purified by three trap-to-trap distillations in nitrogen. In each, generous first and last fractions were blown to waste. The pure liquid was stored at −78° with a slow stream of nitrogen passing through it.

The normal paraffins were freed from olefins by prolonged treatment with 20% oleum. This process also assisted removal of branched-chain isomers, which are more readily sulphonated. The *iso*-paraffins were freed from olefins by successive washings with small volumes of concentrated sulphuric acid until coloration of the acid layer no longer occurred. Subsequent treatment of all the hydrocarbons involved washing with 30% potassium hydroxide solution, then water, partial drying (Na_2SO_4), final drying by refluxing with sodium wire, and fractionation, under nitrogen, through a 60-cm. column, packed with porcelain rings. Refractive indices and b. p. ranges of the materials finally accepted are as shown in Table 1.

TABLE 1.

	n-Pentane	*n*-Hexane	*n*-Heptane	2 : 3-Dimethyl-butane	2 : 2 : 4-Trimethyl-pentane
Boiling range/76 cm.	35—36°	67·5—68·5°	97·5—98·5°	58·2—58·5°	98·5—99·0°
n_D^{20}	1·3586	1·3786	1·3913	1·3756	1·3925

Apparatus.—A flow system was used. The central feature was a Pyrex reaction tube similar to that used in recent investigations of oxidation reactions in this laboratory (Small and Ubbelohde, *J.*, 1953, 637) except that the mixing chamber did not contain Pyrex chips and glass wool, which were found to have an unreproducible effect on chlorination rates. Methods of obtaining reproducible reaction surfaces were also different (see below). For the photochemical experiments, illumination was provided by four 200-watt bulbs, directly above the reaction tube and under an efficient metallic reflector. As it was necessary to run the photochlorinations at >80°, the heating effect of the lamps was supplemented by electrical heating from resistance wire wound directly on to the reaction vessel, at a uniform spacing of 1 cm. between turns. Reaction temperatures were recorded by a thermometer, placed in an axial pocket in the gas flow. In the thermal experiments, the reaction tube was snugly surrounded by an electrically heated steel furnace, from which light was completely excluded.

Chlorine was carried into the reaction vessel by a metered stream of nitrogen, which passed through two saturators in series containing the liquid, held at −78° by an intimate mixture of solid carbon dioxide and alcohol. In calibrating tests, the total amount of chlorine carried through the reaction vessel in a known time was determined by titration of the iodine liberated when the exit gases were passed into potassium iodide solution. Comparison of the analytical results with values calculated from nitrogen flow rates, the vapour pressure of chlorine at −78° (67·5 mm.), and barometric pressure readings indicated that the saturating devices had an efficiency of better than 99%.

Hydrocarbons were carried into the reaction zone as vapours in the same way. For these liquids the carburettors were placed in a thermostat, at temperatures such as to give a partial pressure of 400 mm. for each of the paraffins used. In order to prevent condensation, the parts of the carburettors above the level of the thermostat liquid, and the Pyrex tube connecting the carburettors to the reaction vessel, were electrically heated. Blank experiments with each of the hydrocarbons showed that at least 98% of the calculated volume could be recovered in cooled traps beyond the reaction zone. Flow rates (in c.c./min., calc. at S.T.P.) in photochemical and thermal experiments were : hydrocarbon vapour, 202; chlorine, 22·1; nitrogen, 408. These rates gave a constant contact time of 50·8 secs. with the cross section of reaction vessel used.

Precautions were taken to ensure that chlorination occurred only in the vapour phase and under the controlled conditions in the reaction tube. Thus, light was excluded from all parts of the system beyond the furnace exit ; portions of the collecting train were electrically heated to 150°, which was insufficient to cause thermal chlorination, but sufficient to prevent separation of a liquid phase which might act catalytically in the presence of free chlorine. Immediately before each series of experiments, the reactants were freed from dissolved oxygen by passing nitrogen through the carburettors for 30 min. The chlorine was blown to waste, but the hydrocarbon stream was used to sweep out the reaction tube. At the end of each series of experiments, the reaction vessel was again swept out with nitrogen in order to remove products and reactants. When more exhaustive cleaning of the reaction vessel was desired,

it was washed with alcoholic potassium hydroxide, water, a mixture of nitric and sulphuric acids at 100°, and abundant distilled water, and dried at 200° with a slow stream of nitrogen passing through it (see p. 289).

Collection and Analysis of Products.—When it was sufficient to determine only the chlorine consumed in a particular reaction, the effluent gases were passed through bubblers containing potassium iodide solution. Chlorine which escaped reaction was determined by titration with sodium thiosulphate. The hydrogen chloride formed was determined by addition of excess of potassium iodate, followed by further titration with thiosulphate.

When it was desired to recover organic products, the gases leaving the reaction vessel were freed from chlorine and hydrogen chloride by passing them through a scrubber containing saturated sodium carbonate solution. Usually some organic material collected on the surface of the scrubbing solution, and the remainder was condensed in two traps, cooled in solid carbon dioxide and alcohol. The mixture of unchanged hydrocarbon and alkyl chlorides was separated from the aqueous material, washed twice with water, dried (Na_2SO_4), and fractionally distilled. In most cases the object was to determine the extent to which monochlorides had undergone further chlorination, and therefore the only separation attempted was that of monochlorides from hydrocarbon and polychlorides. The products resulting from the chlorination of *n*-hexane under various conditions were analysed in more detail by methods described below.

Detailed Analysis of the Chlorination Products of n-*Hexane.*—Large volumes of *n*-hexane were chlorinated in a number of experiments. The resulting products contained unchanged hexane (*ca.* 90%), the three monochlorides, and small amounts of polychlorides. It was desired to determine accurately the respective amounts of primary and secondary monochlorides in each mixture.

Preliminary experiments showed that distillation at atmospheric pressure, or prolonged refluxing at reduced pressure, resulted in slight, but probably autocatalytic, decomposition of the chlorides with evolution of hydrogen chloride. This was most undesirable, because of the complicating effect of dissolved hydrogen chloride on the method of analysis to be described. Isolation of the monochlorides was therefore carried out under mild conditions and as rapidly as was consistent with efficient separation. In order to prevent excessive local heating, the boiler was immersed in an oil-bath. The bulk of the unchanged hexane was removed by fractionation at 200 mm. through a column (20 × 2 cm.) packed with glass beads. The fractionation was completed, at 35 mm., by using an efficient column (35 × 1 cm., 15—17 plates) packed with ¼″ glass helices, and operated at a reflux ratio of 15 : 1. The combined monochlorides were collected in the temperature range 35—42°/35 mm. Throughout these fractionations, the boiler contained a small amount of anhydrous sodium carbonate, which was intended to remove hydrogen chloride. Qualitative tests on the recovered solid showed that only a trace of inorganic chloride was formed. The distillate also was free from hydrogen chloride.

Part of each mixture of monochlorides, separated as described above, was analysed by a further fractionation, at atmospheric pressure, the 35-cm. column being used at a reflux ratio of 20 : 1. A fairly satisfactory separation of 1-chlorohexane (b. p. 135—136°) from a mixture of the secondary chlorides (2-, b. p. 125—126°, and 3-chlorohexane, b. p. 123—124°) was obtained, but slight decomposition of the chlorides occurred. Reduced-pressure fractionation

TABLE 2. *Rate constants for reaction* $C_6H_{13}Cl + KI \longrightarrow KCl + C_6H_{13}I$ *in anhydrous acetone at* 60°.

$k = 1/[t(a - b)] \log b(a - x)/a(b - x)$; k in hr.$^{-1}$ mole l.$^{-1}$.

a = original concn. of RCl; b = original concn. of KI; x = KI reacting in t hr (all in mole/l.).

RCl	1-Chlorohexane	2-Chlorohexane	3-Chlorohexane
10^3k	127·4 ($\pm 3 \cdot 7$) [1]	8·2 ($\pm 0 \cdot 3$) [2]	4·4 ($\pm 0 \cdot 2$)

[1] Cf. $10^3k = 125$ (Conant, Kirner, and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 476).
[2] Cf. $10^3k = 7 \cdot 5$ (*idem, ibid.*).

eliminated decomposition but gave a less satisfactory separation. Hence, the fractionation results were used only as confirmation of an independent method of analysis, modified from that described by Hass and Weber (*Ind. Eng. Chem. Anal.*, 1935, **7**, 231) for mixtures derived from *iso*pentane. Analysis was based on the reaction of the monochlorides with potassium iodide in anhydrous acetone. Rate constants at 60° were determined for each of the pure monochlorides (Table 2). The primary chloride reacted much more rapidly than either of the secondary chlorides. Rate constants for mixtures were a linear function of composition

(Fig. 1). From Fig. 1 the respective amounts of primary and secondary chlorides in a mixture of unknown composition can be determined by measurement of the velocity constant. Since the two secondary chlorides do not give quite the same value, the accuracy of the analysis decreases when large amounts of secondary chlorides are present. As used, the method had an accuracy of approximately $\pm 3\%$.

Preparation of Pure Monochlorides.—Specially pure samples of the three monochlorides were prepared by the action of redistilled thionyl chloride on the corresponding alcohols, in the presence of pure pyridine (Darzens, *Compt. rend.*, 1911, **152**, 1314; Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, 77; Vogel, *J.*, 1943, 638). In the synthesis of the corresponding pentane derivatives, this method has been shown to minimise the possibility of rearrangements (Whitmore, Karnatz, and Popkin, *J. Amer. Chem. Soc.*, 1938, **60**, 2540). The secondary alcohols, prepared by the action of aldehydes on the appropriate Grignard reagents, and *n*-hexyl alcohol (B.D.H.) were purified by fractionation at reduced pressure, under nitrogen. The crude chlorides were washed with water and 10% sodium carbonate solution,
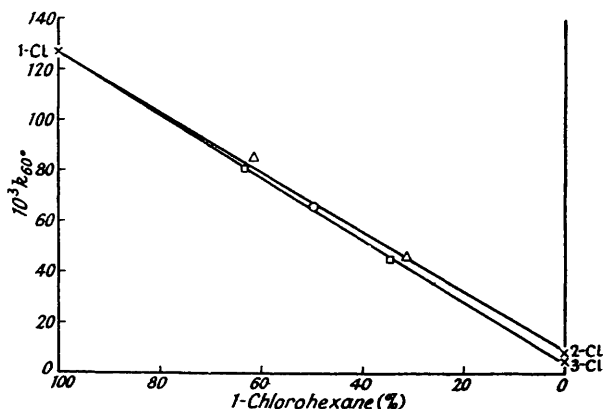

FIG. 1. *Diagram for the analysis of mixtures of the monochlorides from* n-hexane.

× Pure chlorides (1-Cl, 2-Cl, 3-Cl = 1-, 2-, and 3-chlorohexane, respectively).

Synthetic mixtures :
△ 1-Cl + 2-Cl.
□ 1-Cl + 3-Cl.
○ 1-Cl + 2-Cl + 3Cl.

dried ($CaCl_2$), and twice fractionated at reduced pressure. Boiling ranges and refractive indices of the final products, which were completely free from dissolved hydrogen chloride, are shown in Table 3.

TABLE 3. *Characteristics of pure monochlorohexanes.*

	1-Chloro-	2-Chloro-	3-Chloro-
Boiling range	135·5—138°/760 mm.	125—126°/760 mm.	124—125°/760 mm.
	20·0—20·5°/19 mm.	29—30°/24 mm.	23—24°/19 mm.
n_D^{20}	1·4205	1·4162	1·4177

Determination of Rate Constants.—The method devised by Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 232) and followed by Hass and Weber (*loc. cit.*) was used, with several important modifications. Thick Pyrex tubes were used as reaction vessels and each was charged with 5 ml. of 0·04M-potassium iodide (" AnalaR," dried at 110°) in anhydrous acetone (" AnalaR," dried over KOH and redistilled), and a thin glass bulb containing a weighed amount (*ca.* 0·001 mole) of the organic chloride. They were sealed off under nitrogen, fitted with thin sheaths of lead foil to exclude light, and placed in the thermostat at 60° ($\pm 0.05°$) for a preheating period of 1 hr. Reaction was then initiated by breaking the inner bulb against a thick indentation on the bottom of the reaction vessel. After a known time, the residual potassium iodide was determined by titration with 0·003M-potassium iodate, in the presence of hydrochloric acid, the organic halides having first been removed by extraction with chloroform. It was found that a more satisfactory end point was obtained by using only half the volume of concentrated hydrochloric acid suggested by Conant and Kirner (*loc. cit.*).

In preliminary experiments, it was observed that the rate of disappearance of inorganic iodide was greatly increased by the presence of dissolved hydrogen chloride. In such circumstances, the main replacement reaction was accompanied by a side reaction, in which free iodine was produced. Since distillation of the chlorides at atmospheric pressure can result in slight decomposition and contamination of the product with traces of hydrogen chloride, measurements of velocity constants on material so treated are unreliable. Subse-

quently, rigorous precautions, described above, were taken to ensure that all mixtures to be analysed by this method were completely free from hydrogen chloride. With this condition fulfilled, and in the absence of light and oxygen, only the faintest trace of iodine was liberated, even after 48 hours' reaction.

Results.—Conditioning of the surface in thermal chlorinations. When a mixture of hydrocarbon, chlorine, and nitrogen was passed continuously through a " clean " reaction tube, held at a constant high temperature, the proportion of chlorine reacting increased slowly to a steady maximum which was not attained until after 30—60 min. A typical example is shown in Fig. 2. Since oxygen was completely removed from the system before each experiment, this effect must be due to a conditioning of the reaction surface.

After a chlorination there was no appearance of a carbonaceous deposit as reported by Hass, McBee, and Weber (*loc. cit.*) and no other visible change in the condition of the surface of the reaction vessel. However, the reaction surface as produced at *BC* in Fig. 2. was no longer wettable by water or by a mixture of nitric and sulphuric acids at 100°. This indicated that a film had been formed on the surface of the Pyrex glass.

The following properties of this surface film were observed : (i) It could not be removed by prolonged heating in the presence of nitrogen. A reaction vessel in which a chlorination had just been conducted was heated to 300° and kept at this temperature for 5 hr., during which nitrogen was passed over the surface and into a bubbler containing alcoholic silver nitrate solution. The bubbler was changed at hourly intervals, and the contents were examined for
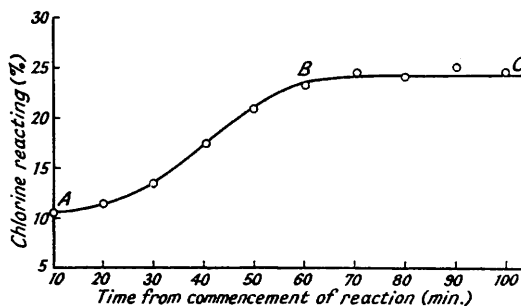

FIG. 2. *Thermal chlorination of* 2 : 2 : 4-*trimethylpentane in a clean vessel at* 219°.

silver chloride. During the first hour a faint turbidity appeared in the silver nitrate solution, indicating that chlorine or a compound containing chlorine had been removed from the reaction surface. Thereafter no further evolution of detectable products occurred and at the end of the experiment the surface was still completely unwettable by water. In effect, the reaction vessel had been purged of adsorbed chlorination products but the main surface film had not been removed by this treatment.

(ii) The film could be removed by exposing the heated reaction surface to oxygen. The vessel which had been treated as in (i) was kept at 300° for 3 hr. in a slow stream of oxygen. The exit gas was tested periodically with alcoholic silver nitrate solution and with Schiff's reagent, but neither chlorine compounds nor aldehydes were detected. However, at the end of the experiment the surface was completely wettable by water. Apparently the main film had consisted of a carbon compound which did not contain chlorine, and could be oxidised to volatile products, probably carbon dioxide and water.

(iii) The surface film could also be removed by washing the reaction vessel with concentrated alcoholic potassium hydroxide solution.
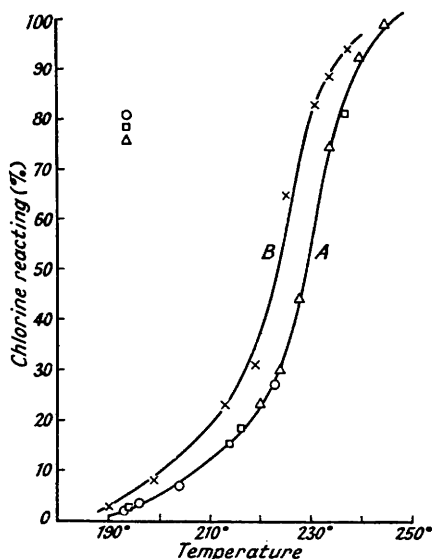
After the initial conditioning of the reaction vessel, described above, high- and low-temperature experiments were completely reproducible provided the reaction vessel was not exposed to oxygen or allowed to cool. A typical temperature profile for the thermal chlorination of *n*-hexane is shown in Fig. 3, Curve *A*. The experimental points were obtained in random order, on different occasions and with several different batches of reactants, but the reaction surface, having first been conditioned was kept at temperatures above 190° throughout the series and was not exposed to the atmosphere. When the reaction surface was cleaned, dried, and again conditioned, a further series of experiments with *n*-hexane gave the results shown in Fig. 3, Curve *B*. Though the temperature profile had the same general shape as before, it was displaced by approximately 6°. Since this effect was also observed in two series of experiments with *n*-pentane, it would appear that it is not possible to obtain absolutely

reproducible surface conditions by cleaning and reconditioning. It may be that the treatment with alcoholic potassium hydroxide not only removes the water-repellent film but also affects the physical properties of the Pyrex surface. A change in the total surface area may be involved.

It was found that the best method of ensuring constant surface conditions over a long period was to restrict the cleaning of the reaction vessel at the end of each run to a thorough purging with nitrogen. The coated surface of a conditiond reaction vessel remained completely unchanged throughout the chlorination of a whole series of paraffins provided it was not allowed to cool or exposed to oxygen. Under these conditions, experiments with different hydrocarbons and at different temperatures were fully reproducible in any order.
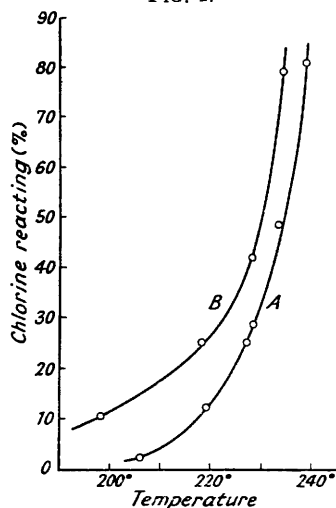
The sensitivity of these reactions to surface conditions was further demonstrated by the accelerating action of Pyrex glass wool. Typical results for *n*-pentane are shown in Fig. 4. This effect was also observed by Vaughan and Rust (*loc. cit.*) in the chlorination of ethane.

FIG. 3.

FIG. 4.

FIG. 3.   *Thermal chlorination of* n-hexane.
Curve *A* : In a " conditioned " vessel; ◯ Series I; ☐ Series II; △ Series III.
Curve *B* : In same vessel after cleaning and " re-conditioning."
FIG. 4.   *Effect of glass wool on the thermal chlorination of* n-pentane.
A, Reaction vessel empty.   *B*, Reaction vessel packed with glass wool.

Effect of molecular structure on relative rates of thermal chlorination.   The C_5—C_8 series of paraffins *n*-pentane, *n*-hexane, *n*-heptane, 2 : 3-dimethylbutane, and 2 : 2 : 4-trimethylpentane were chlorinated under exactly comparable conditions as described in the preceding paragraphs. Results are shown in Figs. 5 and 6 in the form of temperature profiles.

It seemed most likely that the observed differences in reactivity were due only to differences in the molecular structure of the paraffins, but various other possibilities were considered and eliminated. (i) Repeated cross-checking of results showed that surface conditions remained constant throughout the whole series of experiments. (ii) In separate experiments, the organic products resulting from the chlorination of each of the paraffins were collected and examined by fractional distillation. In every case, di- and poly-chlorides constituted less than 5% of the total volume of alkyl chlorides. Therefore the observed differences in reactivity could not have been due to initial chlorination products, from the various paraffins, undergoing further chlorination at different rates. (iii) It was also important to verify that substitution was the chief reaction taking place, since preferential decompositon of certain monochlorides to olefins and hydrogen chloride would have affected the comparisons. A careful examination of the analytical results showed that, over the whole range of temperature investigated, the ratio moles of hydrogen chloride produced/moles of chlorine consumed was

approximately unity, for each of the paraffins. Typical results, for reactions in the neighbourhood of 230°, are shown in Table 4.

TABLE 4. *Equivalence of chlorine consumed and hydrogen chloride produced*
(units : millimoles/min.).

Paraffin	Temp.	Cl_2 entering vessel	Cl_2 recovered unchanged	Cl_2 consumed	HCl produced	$\dfrac{\text{HCl produced}}{Cl_2 \text{ consumed}}$
n-Pentane	226°	0·985	0·747	0·238	0·237	0·995
n-Hexane	231	0·985	0·171	0·814	0·803	0·986
n-Heptane	232	0·985	0·127	0·858	0·863	1·006
2 : 3-Dimethylbutane ...	228	0·985	0·697	0·288	0·296	1·026
2 : 2 : 4-Trimethylpentane	230	0·985	0·520	0·465	0·471	1·013

Since substitution followed by pyrolysis produces two molecules of hydrogen chloride per molecule of chlorine consumed, the close approximation of the ratio to unity indicates that pyrolysis did not occur to any appreciable extent. In the case of 2 : 3-dimethylbutane, the

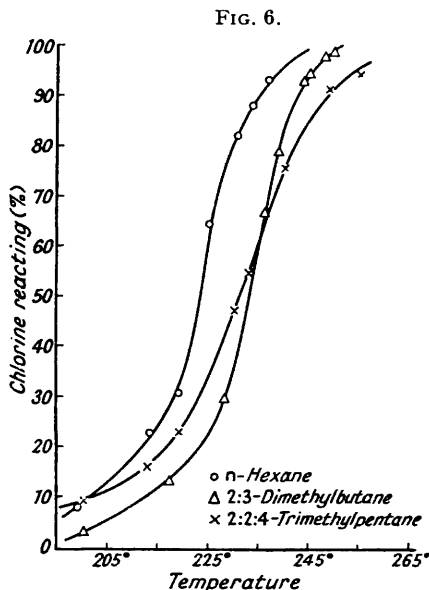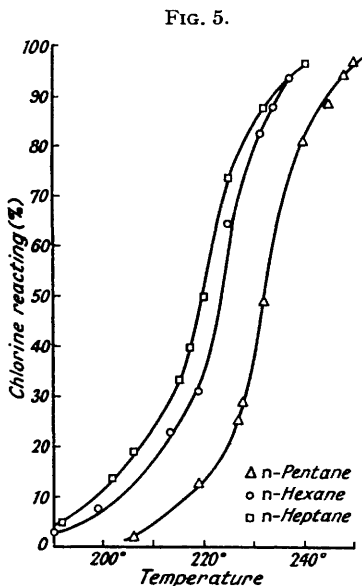FIG. 5.   FIG. 6.

FIG. 5.   *Effect of chain-lengthening on relative rates of thermal chlorination.*
FIG. 6.   *Effect of chain-branching on relative rates of thermal chlorination.*

differences between hydrogen chloride produced and chlorine consumed were just outside the limits of experimental error ($\pm 2\%$), over the whole temperature range, indicating that slight decomposition of the monochlorides of this particular hydrocarbon did occur. However, the amounts of " excess HCl " found were so small that this factor could not materially affect the comparisons. Consequently, the temperature profile was not corrected.

The general conclusion is that the results shown in Figs. 5 and 6 indicate a marked variation in reactivity depending only on the molecular structure of the paraffins.

Photochemical chlorination of n-*hexane.* With the same rates of flow as in the thermal experiments, high percentage conversions of chlorine were obtained by illumination of the reaction tube with white light, at reaction temperatures as low as 80°, which was a lower limit set by vapour-pressure considerations. A typical temperature profile is shown in Fig. 7. Like the thermal reactions, the photochemical process was extremely susceptible to inhibition by oxygen and to surface conditions. The slow build-up to maximum rate in a clean reaction vessel, and the formation of water-repellent surface films were again observed. There was no evidence for decomposition of initial chlorination products, and, as in the thermal reactions, di- and poly-substituted compounds constituted less than 5% of the total volume of alkyl chlorides.

Examination of the chlorination products of n-*hexane.* The object was to determine the

relative amounts of primary and secondary monochlorides produced in reactions at two widely different temperatures, under conditions which otherwise were strictly comparable. Large volumes of the hydrocarbon were chlorinated photochemically at 88°, and thermally at 238°. In both sets of conditions, 94% of the chlorine in the gaseous mixture was being consumed (see Figs. 5 and 7) and monosubstitution was the only important reaction. The mixtures of monochlorides were analysed by the method previously described and the analyses confirmed by fractional distillation. The results are shown Table 5. Since Hass, McBee, and Weber (*loc. cit.*) have shown that the isomeric ratios are unaffected by illumination, the increase of primary halide in the reaction products is apparently due only to the rise in reaction temperature.

TABLE 5. *Analyses of the monochlorination products of* n-hexane.

	Kinetic analysis		Distillation analysis	
Reaction temp.	Primary, %	Secondary, %	Primary, %	Secondary, %
88°	19·8 ($\pm$ 3·0)	80·2 ($\pm$3·0)	25 ($\pm$5)	75 ($\pm$5)
238	24·6 ($\pm$ 3·0)	75·4 ($\pm$3·0)	31 ($\pm$5)	69 ($\pm$5)

DISCUSSION

Surface Effects in Chlorination.—The marked effects of surface conditions on vapour-phase chlorinations have frequently been discussed by previous investigators. Hass, McBee, and Weber (*loc. cit.*) reported induction periods when the reactions were carried out in clean Pyrex glass vessels. They believed that chlorination did not proceed until a " carbonaceous deposit " had been formed. Yuster and Reyerson (*loc. cit.*) experienced great difficulty in obtaining reproducible results in the chlorination of propane and attributed this to variably surface conditions and to the presence of small amounts of oxygen. They also reported the formation of a " brownish substance " on the wall of a reaction vessel in which a series of experiments had been conducted. In the present work, there was no visible change in the condition of the reaction surface but an invisible, water-repellent film was produced. From the results described above, this film consisted of two layers. An adsorbed layer of chlorination products could be removed by thorough purging of the reaction vessel with nitrogen at temperatures slightly higher than those at which the chlorinations were conducted. The main layer was resistant to this treatment but could be removed by the action of oxygen at 300° or by washing the surface with alcoholic potassium hydroxide solution. This hydrolysis, and the absence of any evidence of chlorine compounds during removal of the film by oxidation, suggest that the film is formed by attack of alkyl radicals on the glass surface producing Si–O–R groupings. These are water-repellent and are removed by oxidation or by hydrolysis with alcoholic alkali.

The accelerating action of glass wool also observed by Vaughan and Rust (*loc. cit.*) in the chlorination of ethane indicates that, for the thermal chlorination, chains are initiated on the surface. Pease and Walz (*loc. cit.*) and Yuster and Reyerson (*loc. cit.*) showed that the observed reaction rate could not be explained on the basis of initiation by homogeneous thermal dissociation of chlorine molecules. The change in reaction surface, observed in the present work, suggests a two-fold influence on the rate of chlorination : (i) until the surface has been completely coated with alkyl groups, the rate of reaction is decreased by the removal of chain-carriers in the side-reaction with the glass; (ii) the surface film may be more effective than clean Pyrex glass in initiating chains in the thermal chlorination.

Yuster and Reyerson (*loc. cit.*) reported a progressive decrease in the rate of chlorination when long reaction times were employed, and attributed this to fouling of the surface by highly chlorinated products. In the present dynamic experiments the rate showed no tendency to decrease with time.

Effects of Molecular Structure on Monochlorination Rates.—The main result of the present investigation is that the reaction of chlorine atoms with paraffin hydrocarbons is sensitive to molecular structure. Comparison between *n*-pentane, *n*-hexane, and *n*-heptane indicates clearly that, in this range, the ease of chlorination increases with chain length. The temperature profiles obtained by Vaughan and Rust (*loc. cit.*) for

ethane and propane, and by Topchiev, Krentsel, and Andreev (*Doklady Akad. Nauk S.S.S.R.*, 1952, **85**, 823; *Chem. Abs.*, 1952, **46**, 10,836) indicate that the lower members of the homologous series may be even less reactive than *n*-pentane. This point is illustrated in Fig. 8, but it must be emphasised that strict comparisons between the present and previous work are not possible, since allowance cannot be made for differences in important factors such as surface conditions, size of reaction vessel, contact time, and composition of the gaseous mixtures. However, it does appear that, over the range of *n*-paraffins C_2—C_7 there is a general increase in reactivity towards chlorine as the chain lengthens. A similar effect has been observed by Groll and Hearne (*Ind. Eng. Chem.*, 1939, **31**, 1530) in the chlorination of the series of olefins ethylene, propylene, but-2-ene, and pent-2-ene.

The results shown in Fig. 6 indicate that reactivity is decreased by chain-branching. Under the conditions studied, 2 : 3-dimethylbutane is appreciably less reactive than *n*-hexane. Although *n*-octane has not been studied, it is obvious from the general trend of the results that it would be at least as reactive as *n*-heptane. Yet *iso*octane (2 : 2 : 4-trimethylpentane), over the major part of the temperature range investigated, is appreciably less reactive than *n*-hexane.
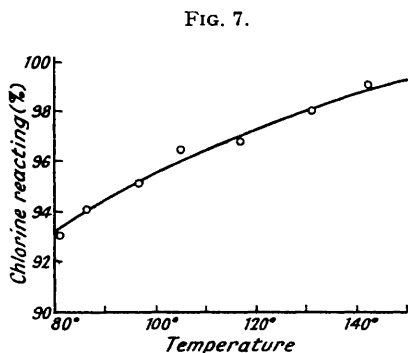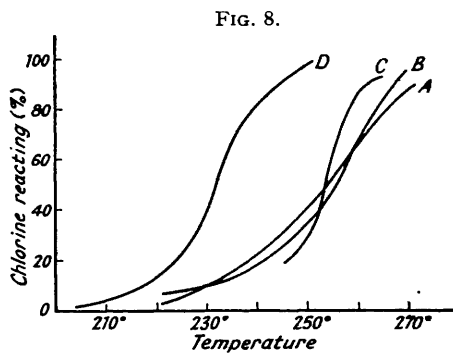
FIG. 7. FIG. 8.

FIG. 7. *Photochemical chlorination of* n-*hexane.*

FIG. 8. *Thermal chlorination of the lower paraffins.*

A, Ethane. *B*, Propane. *C*, *n*-Butane. *D*, *n*-Pentane. (*A*, *B*, from Vaughan and Rust, *loc. cit.* *C*, from Topchiev *et al.*, *loc. cit.* *D*, present work.)

These effects of molecular structure on monochlorination rates are, in some respects, analogous to the effects on rates of slow oxidation below 300°. Although it is again difficult to make strict comparisons, the indications are that in chlorination the effects are not nearly so pronounced as in oxidation. On the basis of the criterion used by Cullis and Hinshelwood (*Discuss. Faraday Soc.*, 1947, **2**, 117) and by Mulcahy (*ibid.*, p. 128), the rate of oxidation, on average, increases by a factor of about 5 for each successive member of the homologous series.

As is shown in Table 6, there is no evidence for differences of this magnitude in vapour-phase chlorination.

TABLE 6.

Paraffin	Cl₂ reacting, %, at :				Paraffin	Cl₂ reacting, %, at :				Paraffin	Cl₂ reacting, %, at :			
	210°	220°	230°	240°		210°	220°	230°	240°		210°	220°	230°	240°
n-Pentane	5	13	37	81	*n*-Hexane	16	40	81	96	*n*-Heptane	23	50	85	96

The same conclusion is reached when the positions of the temperature profiles, for the different paraffins, are compared with minimum temperatures of perceptible combustion, as determined by Callendar (*Engineering*, 1927, **123**, 147).

Differences between chlorination and oxidation are even more pronounced when the effect of molecular branching is considered. For example, Cullis and Hinshelwood (*loc. cit.*) found that the rate of oxidation of *n*-hexane was approximately 1600 times that of 2 : 3-dimethylbutane. Even allowing for the fact that the two systems are far from being strictly comparable, the difference in reactivity between these isomers, observed in the present work, is at the most a factor of 5. Pope, Dykstra, and Edgar (*J. Amer. Chem.*

Soc., 1929, **51**, 1875, 2203) moreover found that the oxidation of 2 : 2 : 4-trimethylpentane required a temperature of 500°, compared with 200—250° for straight-chain paraffins of comparable molecular weight. Yet the chlorination of this compound occurs in the same temperature range as for the other hydrocarbons investigated.

Hypothesis of Independent Reactivity of Different C–H *Bonds.*—At present, the kinetics are too complex to warrant discussion in terms of the highly formalised treatment applicable for simple molecules. Useful discussion of the relations between the reactivities of the different molecules can be made in terms of the simple hypothesis of independent reactivities of the C–H bonds, and of departures from such independent reactivities. Hass, McBee, and Weber (*loc. cit.*) have shown that the rates of substitution at primary, secondary, and tertiary C–H bonds increase in that order. With increasing temperature, the relative rates approach a ratio of 1 : 1 : 1. For purposes of computation the relative reactivities of primary, secondary, and tertiary hydrogen atoms at different temperatures can be taken from figures they supply. At 230° in the vapour phase these are approximately 1 : 3·5 : 5·2. These ratios are not completely independent of the total molecular structure, but in testing the hypothesis this refinement can be temporarily neglected. On the hypothesis of independent reactivities, the respective numbers n_1, n_2, n_3 of primary, secondary, and tertiary C–H bonds in each molecule are multiplied by the appropriate factors and summed over the whole molecule.

Algebraically, Reactivity at 230° = $(n_1 + 3·5n_2 + 5·2n_3)P$, where P is a constant independent of molecular structure but dependent on collision frequencies, etc. Each C–H bond is assumed to react with chlorine atoms or molecules at a rate completely independent of the rest of the structure. *Relative* reaction rates can be expressed very simply on this basis. In Table 7, results of such a series of summations are compared with the observed reaction rates relative to *n*-pentane. Concordance between the calculated and observed sequence of increasing reactivity is sufficiently significant to indicate that a dominant factor in the effect of molecular structure on chlorination rates can be interpreted by the hypothesis of independent bond reactivities.

Co-operative Effects of Molecular Structure on Reactivity.—Although it is doubtful if strictly quantitative comparisons can be made on the basis of this empirical summation, it is noteworthy that *n*-hexane and *n*-heptane appear to be more reactive than would be predicted from the simple additivity rule. This discrepancy would be even more evident if allowance had been made in the calculations for the dependence of the rate factors of secondary hydrogen atoms on overall molecular structure. Thus, even in mono-chlorination, for which the reaction steps seem fairly simple, lengthening the carbon skeleton appears to increase the overall reaction rate above the additive value. Possibly this may be due to vibration-coupling in the unbranched portions of the molecules (Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 354; *Rev. l'Inst. franç. Pétrole*, 1949, **4**, 488). Nevertheless, compared with oxidation of the same hydrocarbons, the overall chlorination rates are much less sensitive to molecular structure.

TABLE 7. *Comparison of calculated and observed rates of thermal chlorination at* 230°.
(Hypothesis of independent bond reactivity.)

| Paraffin skeleton | Calculated Relative rates of substitution of H atoms | | | | Calculated Reaction rate, relative to *n*-pentane | Observed | |
	n_1	$3·5n_2$	$5·2n_3$	Total		Chlorine reacted at 230°, %	Reaction rate, relative to *n*-pentane
C-C-C-C-C	6	21	—	27	(1·00)	37	(1·00)
C-C-C-C-C-C ...	6	28	—	34	1·26	81	2·19
C-C-C-C-C-C-C ...	6	35	—	41	1·52	85	2·30
C-C-C-C (with C,C,C branches)	12	—	10·4	22·4	0·83	37	1·00
C-C-C-C-C (with C,C branches)	15	7	5·2	27·2	1·00	47	1·27

Effect of Chain Length and of Temperature on the Relative Reactivities of Primary and Secondary C–H *Groups.*—As stated above, the relative reactivities of primary and

secondary C–H groups are not strictly independent of the overall structure, or of the temperature.   On the additive hypothesis, in *n*-hexane, the relative reactivity should be
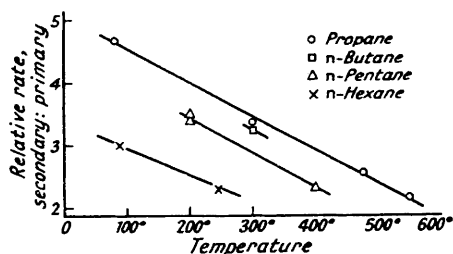
$$\frac{\text{Secondary}}{\text{Primary}} = \frac{\text{Yield of secondary chlorides} \times 6}{\text{Yield of primary chlorides} \times 8}$$

Substitution of the results obtained by the kinetic method of analysis gives 2·30 at 238° and 3·03 at 88°.   Both these figures are smaller than the value 3·5 taken for purposes of illustration in Table 7 and they show a trend towards unity as the temperature rises. Similar trends can be derived from the large body of figures given by Hass, McBee, and Weber, but some care is needed in the selection.   In the present work, the large excess of hydrocarbon and of diluent nitrogen, and the short contact time, ensured that only a small amount of monochloride underwent further chlorination.   Therefore the results are not complicated by preferential removal of certain initial products of chlorination by further reaction.

In Fig. 9 the results now obtained have been compared with those obtained by Hass and his co-workers (*loc. cit.*) for other paraffins, selected for conditions where less than

Fig. 9.   *Effect of chain-lengthening on relative rates of substitution of primary and secondary hydrogen atoms.*

(Values for hexane, present work; others selected from results of Hass, McBee, and Weber, *loc. cit.*)

9% of the reaction products consisted of polychlorides.   It is evident that the reactivity of secondary relative to primary hydrogen appears to decrease as the chain lengthens, when comparisons are made at the same temperature.   The trend is towards unity as the temperature rises, for all the examples given.   This trend with chain length is in excellent agreement with the results obtained by McBee, Hass, and Pianfetti (*Ind. Eng. Chem.*, 1941, **33**, 185) in the chlorination of the series propane, *n*-pentane, and *n*-heptane at a pressure of 1000 lb. per sq. in.   These workers tentatively attributed the trend either to slight differences in activation energies, due presumably to variation in bond energies along the chain, or to steric factors.   Our knowledge of bond energies is still far from complete and hence the former possibility cannot be further discussed.   However, recent physical measurements (McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961; Cummings, McCoubrey, and Ubbelohde, *J.*, 1952, 2725; Cummings and Ubbelohde, *J.*, 1953, 3751) have shown that the normal paraffins, in the range C_5—C_8, are substantially crumpled in the vapour phase.   Consequently, it seems likely that the trend of relative reactivities with chain length observed is due to steric factors.   In partially crumpled configurations, some of the secondary C–H bonds may be protected by other parts of the molecule from attack by chlorine atoms.   This could lead to the observed decrease in relative reactivity of secondary C–H, and the effect would be expected to become more pronounced as the chain lengthened.

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