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Institute of Organoelemental Compounds,
the USSR Academy of Sciences

PRINCIPAL FACTORS IN THE FREE-RADICAL CHLORINATION OF ALKANES

A. S. Bratolyubov

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I. INTRODUCTION

The utilisation of natural and petroleum gases for the heavy organic chemical industry is an important task for the national economy. The huge reserves of gas and petroleum provide the chief raw material for the chemical industry. Saturated hydrocarbons, or alkanes, constitute the bulk of the natural and accompanying gases and a considerable proportion of petroleum, so that the employment of alkanes for organic synthesis is of particular interest. Among the varied processes for their chemical treatment (chlorination, chlorosulphonation, dehydrogenation, oxidation, sulphonation, nitration, etc.) one of the most important is chlorination. This reaction can take place by three different mechanisms depending on the way in which the bond between the atoms in the chlorine molecule is broken.

In the symmetrical, homolytic rupture of the Cl–Cl bond, chlorination subsequently proceeds by a free-radical chain mechanism independently of the method by which the free chlorine atoms were produced (photochemically, thermally, chemically, by means of radiation, etc.)[1-6].

$$\begin{aligned} Cl_2 &\rightarrow Cl\cdot + Cl\cdot \\ Cl\cdot + RH &\rightarrow R\cdot + HCl \\ R\cdot + Cl_2 &\rightarrow RCl + Cl\cdot \text{ etc.} \end{aligned} \qquad (I)$$

Chlorination can take place by an ionic mechanism, the chlorine molecule undergoing heterolytic fission, in the presence of chlorides of metals which are able to form complex ions[7], *e.g.* the chlorides of Fe, Cu, Sb, Sn, Bi, Ti, Al, As, etc.

$$\begin{aligned} FeCl_3 + Cl-Cl &\rightarrow Cl^+[FeCl_4]^- \\ Cl^+[FeCl_4]^- + RH &\rightarrow [RHCl]^+[FeCl_4]^- \\ [RHCl]^+[FeCl_4]^- &\rightarrow RCl + HCl + FeCl_3 \text{ etc.} \end{aligned} \qquad (II)$$

Chlorides of S, I, P, and some other non-metals act in a similar way.

Finally, in the third case

$$Cl_2 + RH \rightarrow RCl + HCl, \qquad (III)$$

chlorination takes place by a bimolecular mechanism, without the formation of free radicals or ions. This mechanism plays an appreciable role at high temperatures (above 400°), when both chlorine and alkane molecules are activated. The weakening of the bonds between the atoms in the molecules makes it possible for the latter to interact directly.

The present paper examines the effects of a number of factors on the chlorination of alkanes by the free-radical chain mechanism.

II. ROLE OF THE MOLECULAR STRUCTURE OF THE ALKANES AND ALKYL CHLORIDES

Molecular structure has a considerable effect on the course of chlorination processes. The optimum conditions for chlorination, and the composition and structure of the resulting products, depend to a large extent on the polarity of the C–H bonds, and to a lesser extent on steric factors. Those hydrogen atoms which are less "protonised" (or more "electronised") in the alkane and alkyl chloride molecules will be more rapidly replaced by chlorine. The state of these H atoms will depend on the strength and character of the effect which the rest of the molecule has on the C–H bond. In the chlorination of alkanes, substitution of the hydrogen atoms depends on the nature of the carbon atom to which they are linked, in the following sequence: tertiary > > secondary > primary[8]. In the gas phase at 300° the relative rates of substitution (or, what is the same thing, the relative reactivities) of these hydrogen atoms are 4.43 : 3.25 : 1.0. The difference in the relative reactivities of hydrogen atoms attached to the three different types of carbon atoms in alkanes results from the different intensities of the positive inductive effect (+*I* effect) exerted by neighbouring alkyl groups on the corresponding C–H bonds[9,10].

As the alkane chain increases in length, the secondary hydrogen atoms increase in number relative to the primary, and this increases both the reactivity of the alkanes towards chlorination and the relative quantities of secondary chlorides and of polychlorides formed. Thus it is clear from Fig. 1 that, at a given temperature, a greater proportion of the chlorine reacts in the thermal chlorination of heptane than in that of hexane or of pentane[11]. The chlorination of methane, ethane, propane, and butane supports this rule[12,13]. Table 1 gives the proportions of primary and secondary chlorides formed in the chlorination, under conditions which avoid polychlorination or pyrolysis, of n-alkanes containing different numbers of carbon atoms[14].

The relative reactivity of hydrogen atoms linked to primary, secondary, and tertiary carbon atoms in an alkane is not constant but is greatly affected by the chlorination temperature and the nature of the solvent. The presence of moisture, charcoal, catalysts, or light, however, has no great effect[8].

The relative reactivities of the hydrogen atoms change markedly during the polychlorination of alkanes, owing to the inductive effect of the chlorine atoms which have entered the molecule.

Thus a study of the liquid-phase chlorination of 1-chlorobutane, 1,1-dichlorobutane, and 1,1,1-trichlorobutane has shown that the chlorine which has entered the molecule deactivates the C–H bonds of its immediate neighbours, and this effect is intensified by increasing the number of chlorine atoms in position 1 in the alkane molecule. Table 2 shows that even the presence of one chlorine atom deactivates position 2, while having little effect on position 3. The presence of two or more chlorine atoms in position 1 is sufficient to deactivate position 3 as well[15].

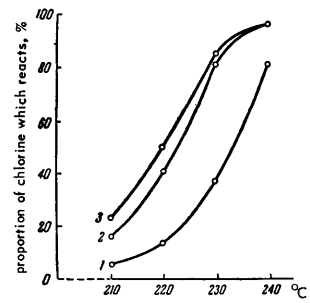


Fig. 1. Effect of chain length on relative rates of thermal chlorination of alkanes:
1) n-pentane; 2) n-hexane; 3) n-heptane.

TABLE 1. Effect of chain length of alkanes on composition of monochlorides.

No. of C atoms in molecule	Primary chlorides, %	Secondary chlorides, %	No. of C atoms in molecule	Primary chlorides, %	Secondary chlorides, %
3	50.0	50.0	12	8.5	91.5
4	33.0	67.0	20	4.9	95.1
5	23.5	76.5	25	3.9	96.1
6	18.7	81.3	30	3.2	96.8
10	10.3	89.7			

In the chlorination of 1-chlorobutane the relative reactivity of the hydrogen atoms in position 2 is found to be half the value for position 3 (3.2 and 6.7 respectively). In the 1,1-dichlorobutane molecule the relative reactivity of hydrogen in position 2 is one-quarter of that for position 3 and one-half of that for hydrogen in position 4 (the respective values being 3.0, 12.3, and 6.2).

TABLE 2. Effect of chlorine atoms on reactivity of hydrogen atoms in n-butane.

Position of Cl atom	C(4) – C(3) – C(2) – C(1) – X				
% substituted on chlorination	27	47	22	7	Cl (1-chloro)
Relative reactivity of H atom	2.6	6.7	3.2	1	
% substituted on chlorination	37	49	12	2	Cl_2 (1,1-dichloro)
Relative reactivity of H atom	6.2	12.3	3.0	1	
% substituted on chlorination	51	49	0	0	Cl_3 (1,1,1-trichloro)
Relative reactivity of H atom	1	1.4	0	0	

The deactivation of the C–H bonds is a result of the negative inductive (*-I*) effect of the chlorine atom which has already replaced one of the hydrogen atoms (a particular case of the "vicinal effect"[16-19]).

In the presence of a chlorine atom not located on a terminal carbon atom the greatest relative reactivity is shown by the hydrogen atoms which are farthest removed from the negative substituent (chlorine) and are under the influence of the *+I* effect of the alkyl groups. The *-I* effect of the chlorine atom is much greater in magnitude than the *+I* effect of the alkyl groups. Therefore the reactivity of hydrogen atoms is numerically much smaller in alkyl chlorides than in alkanes, and it decreases still further as chlorine atoms accumulate in the molecule. Thus the reactivities of the hydrogen atoms in butyl chloride, methylene chloride, and chloroform are 12%, 1.1%, and 0.5% of the reactivity of a methyl hydrogen atom in n-heptane. The reactivity of the hydrogen atom in chloroform is 0.12% of that of a hydrogen atom in position 2 in 2,3-dimethylbutane[20].

Owing to the deactivation of the hydrogen atoms in alkyl chlorides, the latter undergo chlorination less readily than do the alkanes. Methane is an exception to this rule, as it is more difficult to chlorinate than is methyl chloride[21].

III. EFFECT OF SOLVENTS

It is usually considered that solvents have a negligible effect on the velocity and course of competing free-radical chain reactions, in particular on chlorination[22,23]. Recent research[20,24,25] has shown, however, that the solvent does not act merely as a reaction medium. Solvents can change the direction of the process and the composition of the chlorination products. Thus at 25° the photochemical chlorination of pure 2,3-dimethylbutane gives 60% of 1-chloro-2,3-dimethylbutane and 40% of 2-chloro-2,3-dimethylbutane. In the presence of 12 M carbon disulphide, however, the 2-chloro compound constitutes 97.4% of the total yield of chloro-2,3-dimethylbutanes[20]. The observed relative reactivity of the methylidyne hydrogen atom has thus increased from 4 to 225. When n-heptane is chlorinated under the same conditions, the relative reactivity of a methylene hydrogen atom is observed to increase from 3.7 to 29.0. The effect of solvents has been most fully studied in the photochlorination of 2,3-dimethylbutane[20,24] (see Table 3).

It is seen from Table 3 that aromatic solvents generally exert a fairly strong influence on the observed relative reactivities of the hydrogen atoms. Most non-aromatic solvents have only a feeble effect in this case. The difference is evidently associated with the differing abilities of these types of solvents to solvate the highly electrophilic chlorine atom to form complex compounds of different reactivity[20,24]. The more stable the resulting complexes, and hence the lower their reactivity, the greater is the selectivity of the chlorine atom combined in the complex. From the electronic point of view, this is a result of the decrease in the electrophilic character of the coordinated chlorine atom, the effect becoming more marked as the stability of the complexes increases. This diminution in electrophilic properties and the associated lower activity of the chlorine atom in the complex makes it difficult or impossible to remove the more "protonised" hydrogen atom of the alkane. Fig. 2 illustrates the effect of complex-forming solvents on the chlorination of alkanes[25]. The energy relationships of reactions involving free chlorine atoms have been calculated from data on the gas-phase reactions and the known bond dissociation energies. The energetics of reactions involving chlorine atoms combined in complexes are more sketchy, but they do show both the origin of the greater selectivity and the greater effect of temperature. Investigation of the kinetics of the chlorination of 2,3-dimethylbutane in the presence of solvents has shown[20] the presence of a dynamic equilibrium between free and coordinated chlorine atoms, the relative proportions being 1 : 10.4 with 8 M benzene as solvent at 25°. The free chlorine atom replaces hydrogen atoms attached to a primary as well as those attached to a tertiary or a secondary carbon atom. Thus the composition of the chlorination products of an alkane and the observed relative reactivity of the hydrogen atoms depend on the relative proportions of chlorine atoms which are free and which are coordinated with the solvent.

When aromatic solvents are involved, the highly electrophilic chlorine atom forms complex compounds by association with the π electrons of a double bond in the aromatic nucleus. Aromatic solvents containing electronegative substituents (nitrobenzene, chlorobenzene, fluorobenzene, trifluoromethylbenzene) have only a slight effect.

TABLE 3. Effect of solvents on the observed relative reactivity of a hydrogen atom attached to a tertiary carbon atom in 2,3-dimethylbutane.

Non-aromatic solvents (concn. 4 M)	Relative activity at 55°	Aromatic solvents (concn. 4 M)	Relative activity at 55°
2,3-Dimethylbutane	3.7	Nitrobenzene	4.9
		9-n-Butylanthracene (2 M)	5.0
Nitromethane	3.3	Benzoyl chloride	6.4
Chloroform	3.5	Trifluoromethylbenzene	6.9
Cyclohexene	3.6	Methyl benzoate	10.2
Trichloroethylene	3.6		
Silicon tetrachloride	3.7	Chlorobenzene	10.2
Propionitrile	4.0	Fluorobenzene	10.3
Butyric acid	4.1	Thiophen	13.3
Methyl acetate	4.3	Benzene	14.6
Butyl alcohol	4.8	*o*-Xylene	15.0
Dioxan	5.6	Toluene	15.4
Butyl ether	7.2	Ethylbenzene	16.3
Thionyl chloride	7.3	Anisole	18.4
NN-Dimethylformamide	9.1	*p*-Xylene	18.6
Sulphur monochloride	14.0	Cumene	20.3
Carbon disulphide	33.0 (25°)	*m*-Xylene	22.4
Butyl iodide	390	Butylbenzene	24.0
Ethyl iodide	600	Mesitylene	25.0
		2-Isobutylnaphthalene	30.0
		Iodobenzene	31.0
		1-Chloronaphthalene	33.0

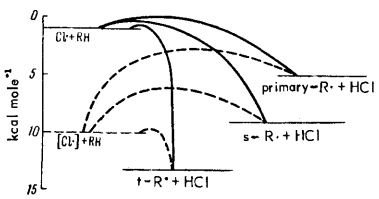
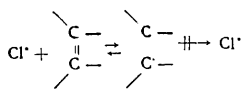


Fig. 2. Energetics of reactions of coordinated and free chlorine atoms with alkanes.

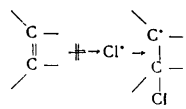
In contrast, those containing electron-donor substituents (butylbenzene, mesitylene, cumene, *m*-xylene) exert a considerable influence on the observed relative reactivity towards chlorination of the hydrogen atoms in alkanes.

The polarisability of the substituent is of immense importance. When it is high, complexes of great selectivity are formed. It is seen from Table 3 that solvents containing the readily polarisable sulphur and iodine atoms (sulphur monochloride, carbon disulphide, butyl iodide, ethyl iodide, iodobenzene) have a very marked effect on the composition of the chlorination products obtained from alkanes. However, it is undesirable to employ solvents having an unnecessarily high capacity for solvating electrophilic molecules, owing to the formation of unreactive complexes. Thus compounds containing an ethylenic bond (cyclohexene, trichloroethylene) and anthracene compounds (9-n-butylanthracene) have no appreciable effect on the observed relative reactivities of the hydrogen atoms in the chlorination of 2,3-dimethylbutane.

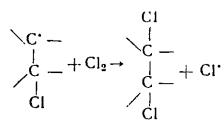
The π complexes formed in this case,



are rapidly converted into σ complexes,



with the ultimate formation of products in which the chlorine has been added to a double bond in the solvent molecule:



In this case the hydrogen atoms in the alkane are split off only by a free chlorine atom, so that there is no effect of the solvent on the observed relative reactivities of the hydrogen atoms towards chlorination.

The equilibrium between free and coordinated chlorine atoms, and hence the observed relative reactivities of the hydrogen atoms, are considerably affected by the temperature and especially the concentration of the solvent. Fig. 3 shows[25] that, with a carbon disulphide concentration of 11.1 M, an increase in the chlorination temperature from 0° to 68° reduces the observed relative reactivity of a methylidyne hydrogen atom in 2,3-dimethylbutane from 93.2 to 34.0, *i.e.* by a factor of 2.7. The same rise in temperature in the absence of the solvent results in a fall in relative reactivity from 4.9 to 4.0, *i.e.* by a factor of only 1.2. The chlorination of n-butane follows a similar pattern, chlorination under the same conditions showing a decrease in relative reactivity of a hydrogen atom attached to a secondary carbon atom by a factor of 2.0 in the presence of solvent, compared with 1.1 without a solvent[25]. The concentration of the solvent has a still greater effect, Fig. 4 showing that an increase in the carbon disulphide concentration from 2 M to 12 M involves an increase in the observed relative reactivity of a methylidyne hydrogen atom at 2,3-dimethylbutane from 15.0 to 225.0.[20]

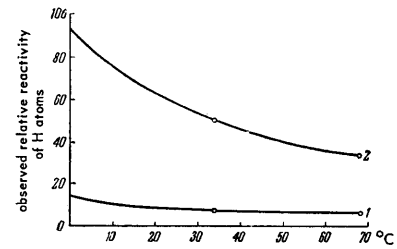


Fig. 3. Effect of temperature on observed reactivity of hydrogen atoms (relative to those attached to primary carbon atoms in the same compound) in the presence of 11.1 M carbon disulphide:
1) activity of hydrogen atoms attached to secondary carbon atom in n-butane;
2) activity of hydrogen atoms attached to tertiary carbon atom in 2,3-dimethylbutane.

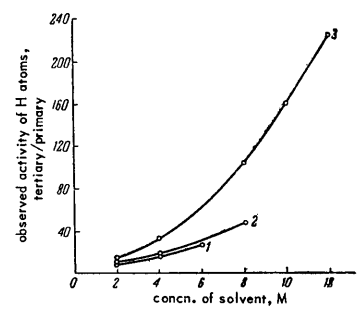


Fig. 4. Effect of concentration of different solvents on observed relative activity of hydrogen atom in 2,3-dimethylbutane at 25°:
1) chlorobenzene; 2) benzene; 3) carbon disulphide.

Up till now we have been concerned mainly with the effect of the reactivity of the coordinated chlorine atom on the composition of the chlorination products. In the chlorination of alkyl chlorides, however, solvents which readily solvate electrophilic molecules have also a direct effect on the reactivity of the hydrogen atoms of C–H bonds. Thus the reactivity of a hydrogen atom in methylene chloride towards photochlorination in the absence of solvent is 0.3% of the reactivity of a methylene hydrogen in n-pentane, whereas in the presence of 12 M carbon disulphide the corresponding figure is 1.2%, a fourfold increase[20]. When chloroform is chlorinated under analogous conditions, the reactivity of the hydrogen atom increases nearly sevenfold from 0.12% to 0.8% of the reactivity of a hydrogen atom attached to a tertiary carbon atom in 2,3-dimethylbutane[20].

The increased reactivity of hydrogen atoms attached to carbon atoms in these and similar cases is evidently a result of solvation, not only of the free chlorine atom, but

also of the molecule of alkyl chloride undergoing chlorination. Solvation of the latter by electron-donor solvents decreases the *-I* effect of the chlorine atom, and hence increases the reactivity of the hydrogen atoms during chlorination[20,26].

IV. EFFECT OF TEMPERATURE

The chlorination of the lower alkanes has been investigated at temperatures up to 1000° and above[8,12,27-30].

Methane, ethane, propane, and the butanes yield considerable amounts of chloro-derivatives even at 300°. As already noted, temperature exerts a marked effect on the process and on the composition of the products. As the temperature rises, the relative reactivities of the different hydrogen atoms become increasingly similar.

Thus the vapour-phase photochlorination of propane at 80° yields 61.5% of 2-chloropropane and 38.5% of 1-chloropropane. When the reaction temperature is raised to 600° the corresponding yields are 42.2% and 57.8% respectively. The relative reactivity of the methylene hydrogen atom has fallen[8] from 4.7 to 2.2.

The chlorination of isobutane under similar conditions shows a decrease in the yield of 2-chloro-2-methylpropane from 45.3% to 23.5% of the total quantity of monochlorides obtained. The reactivity of hydrogen attached to a tertiary carbon atom relative to that of a primary hydrogen falls in this case[8] from 7.4 to 2.8. The relative reactivities of the hydrogen atoms are more sensitive to a change in temperature in liquid-phase than in gas-phase chlorination. Thus, in the liquid-phase photochemical chlorination of propane, a rise in temperature of 90° (from -60° to +30° in CCl_4 medium) is accompanied by a diminution in the relative reactivity of a methylene hydrogen atom from 8.3 to 3.2, *i.e.* by a factor of 2.6, whereas in the gas-phase thermal chlorination an increase in temperature of 300° (from +300° to +600°) entails a fall in relative reactivity from 3.2 to 2.2, *i.e.* only by a factor of 1.4.

Given relative reactivities of the hydrogen atoms in alkanes are reached at considerably lower temperatures in liquid-phase than in gas-phase chlorination. Thus it can be seen from the preceding example that a relative reactivity of 3.2 for a methylene hydrogen atom in propane is reached at +30° in the case of liquid-phase chlorination, whereas a temperature of +300° is necessary with gas-phase chlorination. The chlorination of isobutane shows a similar pattern[8].

The effect of temperature on the relative reactivities of hydrogen atoms in the chlorination of alkanes, the general picture of which is illustrated in Fig. 5, is apparently explained by the different stabilities of the alkyl chlorides[8]. The stability falls in the sequence primary > > secondary > tertiary, which leads to a corresponding change in relative rates of substitution of the hydrogen atoms, and hence in their relative reactivities, when the temperature is raised. Steric factors probably play an important part at low temperatures, especially in liquid-phase chlorination. Owing to the decrease in kinetic energy in the liquid phase when the temperature drops, the vibrations of the C–C links in the alkane chains also diminish. The alkane molecules take up the energetically most favourable form, which is less bent and more extended. The screening of some of the C–H bonds involving secondary or tertiary carbon atoms by other parts of

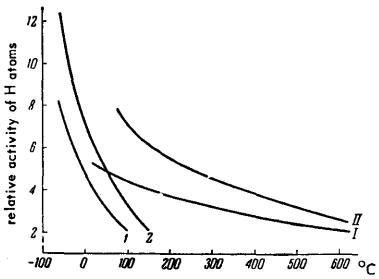


Fig. 5. Effect of temperature on relative activities of hydrogen atoms attached to different carbon atoms in alkanes:
1) secondary C/primary C } in liquid phase
2) tertiary C/primary C }
I) secondary C/primary C } in vapour phase
II) tertiary C/primary C }

the molecule decreases. This leads to an increase in the observed relative reactivity of the hydrogen atoms attached to secondary or tertiary carbon atoms[31-35].

It follows from Fig. 5 that the maximum yield of primary chlorides is achieved at high temperatures, and the maximum yield of secondary or tertiary chlorides at low temperatures. This makes it possible to control the chlorination and to obtain preferential formation of either primary or secondary and tertiary alkyl chlorides. Table 4 shows that, in the vapour-phase thermal chlorination of the C_6–C_{10} alkanes, the temperature for preferential formation of primary monochlorides is 120°–160° above that for preferential formation of secondary monochlorides[36,37]. 1-Chlorohexane (at 197°) and 2-chlorohexane (at 77°) can be obtained in yields of 71% and 75% of theoretical. Polychlorination increases as the hydrocarbon chain becomes longer, which entails some decrease in the yield of monochlorides, and raises the optimum temperature for obtaining the latter.

Vigorous formation of polychlorides begins above 500°, and is due not so much to further chlorination of monochlorides as to the chlorination of pyrolysis products. However, the formation of polychlorides can be reduced to a minimum by the use of high bulk rates of flow, which shorten the time during which the reaction products and the initial alkanes remain in the high-temperature zone[8].

TABLE 4. Yield of isomeric monochlorides at the optimum temperatures for chlorination and at an alkane : chlorine molar ratio of 10 : 1.

Normal alkane	Primary alkyl chlorides predominant		Secondary alkyl chlorides predominant	
	optimum temp., °C	yield of primary monochloride, % of alkane chlorinated	optimum temp., °C	yield of secondary monochloride, % of alkane chlorinated
Hexane	197	71.0	77	75.0
Heptane	257	67.0	137	73.7
Octane	277	60.3	177	69.2
Nonane	317	58.3	187	64.7
Decane	357	55.0	197	61.2

As the temperature rises above 300° the rate of 1,1 and 1,1,1 chlorination increases, while that of chlorination in the 1,2 position falls. Thus although chlorination of ethane at 320° yields 1,1-dichloroethane and 1,2-dichloroethane in the proportions 4 : 1 with no 1,1,1-trichloroethane, at 415° the relative proportions of these three products are [8,12] 18.5 : 1.0 : 2.4. The distortion of the orienting influence of the chlorine is due to the free-radical character of thermal chlorination. Among the possible chlorination products, the one derived from the intermediate hydrocarbon radical which is the most stable at the given temperature is formed preferentially.

The stabilities of hydrocarbon radicals decrease in the sequence tertiary > secondary > primary [38]. When, therefore, the temperature of chlorination is increased beyond a certain limit (which is quite definite for any given alkane), the composition of the reaction products is displaced towards the formation of 1,1- and 1,1,1-chloro-derivatives. The unstable free radical of the type $\cdot CHR.CH_2Cl$ which is formed exhibits a tendency to stabilise itself by splitting off the chlorine atom to form an olefine. The chlorination of alkyl chlorides can be represented by the following general equations [15]:

$$\left.\begin{array}{l} \\ \\ \end{array}\right| \begin{array}{l} R-CH_2-CH_2Cl + Cl^{\cdot} \xrightarrow{-HCl} R-CH_2-CHCl \xrightarrow[-Cl^{\cdot}]{+Cl_2} R-CH_2-CHCl_2, \quad (a) \\ \rightarrow R-\dot{C}H-CH_2Cl \rightleftharpoons R-CH=CH_2 \xrightleftharpoons[-Cl^{\cdot}]{+HCl} R-CHCl-CH_3, \quad (b) \end{array}$$

$$\begin{array}{l} \quad\quad\quad\

Effect of nitrogen trichloride. Technical chlorine always contains nitrogen trichloride which, in spite of its minute concentration (of the order of 0.001%), undoubtedly has an appreciable effect on the chlorination of alkanes at moderate temperatures. The effect of nitrogen trichloride is due to the reaction[41]

$$Cl^{\cdot} + NCl_3 \rightarrow NCl_2 + Cl_2.$$

The energy of the N–Cl bond is about 20 kcal smaller than that of Cl–Cl, and as a result the regeneration of chlorine atoms by the reaction

$$NCl_2 + Cl_2 \rightarrow NCl_3 + Cl^{\cdot} - 20 \text{ kcal},$$

is extremely slow at room temperature. The destruction of the active chlorine atoms leads to inhibition of the chain process.

A study of the photochemical chlorination of hydrogen has shown that a given retardation can be produced by a concentration of nitrogen trichloride which is only 10^{-5} of the oxygen concentration required. At high temperatures, on the other hand, nitrogen trichloride accelerates the chlorination owing to its decomposition to form free chlorine atoms

$$2NCl_3 \rightarrow N_2 + 6Cl^{\cdot}.$$

Effect of catalysts which act as chlorine carriers. Among these we are concerned most often with the effect of iron salts, which under the conditions of purely chain (*e.g.* photochemical) processes of chlorination retard the reaction[44]. The inhibiting effect of iron salts is evidently a result of interaction between the alkyl radicals which are formed and ferric ions, with reduction of the latter to the ferrous state[45]

$$R^{\cdot} + Fe^{3+} + Cl^{-} \rightarrow RCl + Fe^{2+},$$

$$Cl_2 + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2Cl^{-}, \text{ etc.}$$

The harmful effects of iron salts can be eliminated by adding 0.1–1% of a phosphoric ester or of some other organic compound of phosphorus which will convert iron salts into complex compounds. The presence of water has a similar though less marked effect, as it deactivates the salts by hydrating them[46]. Under certain conditions, however, iron salts can initiate free-radical chain processes. Thus in the absence of light and initiators, $FeCl_3$ is able to catalyse the chlorosulphonation of alkanes[47], which, in contrast to chlorination processes, takes place only by a free-radical mechanism[48]:

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl,$$

$$R^{\cdot} + SO_2 \rightarrow RSO_2^{\cdot}; \quad RSO_2^{\cdot} + Cl_2 \rightarrow RSO_2Cl + Cl^{\cdot}, \text{etc.}$$

The activation of free-radical chain processes by ferric chloride is evidently due to the exothermic nature of the ionic chlorination of alkanes which occurs under its influence. The energy evolved in this process is partly dissipated as heat and partly used up in the dissociation of a chlorine molecule to form free atoms:

$$RCl^{*} + Cl_2 \rightarrow RCl + Cl^{\cdot} + Cl^{\cdot}.$$

The free chlorine atoms which are formed now enable chlorination and chlorosulphonation to take place as chain reactions[14,49]. Other catalysts which are chlorine carriers have an effect analogous to that of ferric chloride. Like the latter, they are able under certain conditions to inhibit or to catalyse free-radical chain reactions. A study of the chlorosulphonation of n-heptane and of isooctane at 35°–40° in the absence of light and initiators has shown that the catalysts used could be arranged in the following sequence of decreasing activity[14]:

$$S > PCl_5 > SbCl_5 > I_2.$$

When n-heptane is chlorosulphonated in the presence of sulphur the yield of heptanesulphonyl chlorides is 17% of theoretical, compared with 45.3% in the photochemical process. The formation of one mole of monochlorides of heptane is accompanied by the formation of 2.5 moles of heptanemonosulphonyl chlorides. The chlorosulphonation of isooctane under the same conditions yields 21.1% of monosulphonyl chlorides compared with 21.2% in the photochemical process, the formation of one mole of monochlorides of isooctane being accompanied by that of 1.55 moles of isooctanemonosulphonyl chlorides[14].

The fact that in the presence of these catalysts the yield of sulphonyl chlorides is proportional to the amount of chlorides formed is a direct indication that the free-radical chain reactions occurring under these conditions are dependent on processes of ionic chlorination.

2. Impurities which Induce Free-Radical Chain Processes of Chlorination

Effects of SO_2 and NO_2. Sulphur dioxide and nitrogen dioxide have an appreciable effect on chain processes. Both thermal and photochemical chlorination of alkanes are considerably accelerated in the presence of SO_2, as well as in the presence of initiators for chain reactions[30]. The chlorination of alkanes in also considerably accelerated in the presence of NO_2. Thus with n-butane and an addition of 2% of NO_2 at 150° the amount of chlorine consumed is 44%, whereas in the absence of NO_2 there is practically no reaction at this temperature[50]. Very little work has been done on this phenomenon, which is apparently explained by SO_2 and NO_2 acting as intermediate links in the chain reaction. This reduces to a minimum the processes by which chains, once started, are terminated, and lengthens their life. The following is a possible example of a chain reaction involving SO_2:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2,$$

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl,$$

$$R^{\cdot} + SO_2Cl_2 \rightarrow RCl + SO_2Cl^{\cdot},$$

$$SO_2Cl^{\cdot} \rightarrow SO_2 + Cl^{\cdot}, \text{ etc.}$$

When NO_2 is used, direct initiation of the chain reaction may also occur, the nitrogen dioxide displaying its latent radical character[41,51]

$$NO_2 + RH \rightarrow R^{\cdot} + HNO_2,$$

$$R^{\cdot} + Cl_2 \rightarrow RCl + Cl^{\cdot};$$

$$Cl^{\cdot} + RH \rightarrow R^{\cdot} + HCl, \text{ etc.}$$

Effect of olefines. The catalytic action of small amounts of olefines on the chlorination of alkanes is of great practical interest. Thus it has been shown that, in the absence of light and other impurities, the chlorination of propane, butane, and pentane is greatly accelerated in the presence of ethylene[52,53]. When liquid n-butane is chlorinated in the presence of but-2-ene, the formation of one mole of 2,3-dichlorobutane is accompanied by the substitution of chlorine for hydrogen in ten moles of the n-butane[52]. It follows from this that the additive chlorination of olefines can induce the chlorination of alkanes. In

the presence of traces of some metal salts, the former takes place by an ionic mechanism. The energy evolved in the chlorination of, for example, ethylene

$$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 58 \text{ kcal mole}^{-1},$$

as in the case of the inducing effect of catalysts which are chlorine carriers, causes the molecular chlorine to dissociate into free atoms:

$$C_2H_4Cl_2^* + Cl_2 \rightarrow C_2H_4Cl_2 + Cl^{\cdot} + Cl^{\cdot}.$$

The free-radical chain processes involved in the chlorination of alkanes then proceed in the usual way. The above mechanism for the inducing effect of olefines is confirmed by the ability of olefines to catalyse free-radical chain processes in the chlorosulphonation of alkanes. Thus the chlorosulphonation of n-heptane in the presence of ethylene and in the absence of light and other impurities goes very smoothly at 45° with a yield of heptanemonosulphonyl chlorides which is ~45% of theoretical[14]. An unnecessarily high content (20% or more) of olefines in the hydrocarbon mixture and the use of too low reaction temperatures (which are quite definite with each particular olefine) are undesirable, since the additive chlorination then becomes the main consumer of the chlorine, and the chlorination of the alkanes is retarded[54]. The presence of oxygen has a detrimental effect on the olefine-induced chlorination of alkanes, which is readily understood from the chain character of chlorination and chlorosulphonation processes.

Effect of initiators. Chain initiation is the most difficult step in the chlorination chain reaction, although the energy of rupture of the C–H bond in different alkanes and especially in alkyl chlorides is of some significance. Dissociation of the original molecules into two free radicals or atoms is the simplest way in which the initial radicals can be formed. Comparing the energy of the Cl–Cl bond (57.2 kcal mole^{-1}) with those of C–H and C–C in alkanes (85–101 and 60–83 kcal mole^{-1} respectively) we see that, in the alkane–molecular chlorine system, the latter dissociates the more readily to form active species. However, even the dissociation of molecular chlorine requires quite severe treatment, such as temperatures of 300° and above, light quanta, exposure to radioactive materials, or X-rays[41,55]. Therefore, the presence of initiators, whose molecules dissociate into free atoms and radicals more readily than molecular chlorine, is of great importance in free-radical chain chlorination processes. Among such substances are other halogens, alkali metals, organometallic compounds, organic peroxides and hydroperoxides, azo and diazo compounds, tetrazens, disulphides, arylethanes, etc. However, the effectiveness of initiators is determined not only by the readiness with which they decompose but also by the reactivity of the resulting free atoms or radicals. In other words, an initiator will be highly effective only if the low energy required for its decomposition into free radicals or atoms is complemented by a fairly high energy of bonding of the latter in the reaction products. Thus the energy of dissociation of molecular iodine into free atoms is 35.5 kcal mole^{-1}, compared with 57.2 kcal mole^{-1} for molecular chlorine[41]. However, the free atoms of iodine formed by the dissociation of I_2 are not very active, and are unable to split off a hydrogen atom from an alkane molecule, since the energy of the H–I bond is less than that of C–H (70.5 and 85–101 kcal × × mole^{-1} respectively). The reaction

$$I^{\cdot} + Cl_2 \rightarrow ICl + Cl^{\cdot},$$

is also energetically unfavourable, since the energy of the I–Cl bond is less than that of Cl–Cl (49.8 and 57.2 kcal × × mole^{-1} respectively).

Furthermore, in the presence of I_2 free chlorine atoms which have been formed in some other way react, not with the alkane, but with molecular iodine,

$$Cl^{\cdot} + I_2 \rightarrow ClI + I^{\cdot},$$

since the I–I bond is considerably weaker than C–H: *i.e.* under certain conditions I_2 can act as an inhibitor of chain chlorinations. Such very active initiators as fluorine, alkali metals, and organometallic compounds of the alkali and alkaline-earth metals are seldom employed because their great chemical reactivity makes their practical application difficult. Fluorine occupies a special position among all other initiators because the relatively high energy of the F–F bond (37.6 kcal mole^{-1}) cannot be reconciled with the exceptionally large effect of fluorine at low temperatures on the basis of dissociation into free atoms. Chlorination of ethane in the presence of fluorine at room temperature and below gives a 90–100% yield of ethyl chloride and dichloroethane, with the whole of the chlorine reacting[56].

The action of fluorine on chlorination processes apparently consists in the formation of free radicals by reaction with the alkane:

$$F_2 + RH \rightarrow R^{\cdot} + F^{\cdot} + HF.$$

The unusual behaviour of fluorine is due to the fact that the resulting H–F bonds are very stable compared with the F–F bonds (bond energies 134 and 37.6 kcal mole^{-1} respectively). Owing to this, the reaction of fluorine with an alkane is characterised by a negligible activation energy (a few kilocalories per mole), and involves practically no consumption of energy: *i.e.* it is either thermoneutral (with methane) or exothermic (with other alkanes and with alkyl chlorides). The extraordinarily great activity of fluorine in reactions with other organic compounds is due to the above factors, as has been suggested[41].

The initiating action of alkali metals has been most fully investigated in the chlorination of hydrogen[41]. Addition of sodium vapour (energy of Na–Na bond 17.5 kcal × × mole^{-1}) to a mixture of chlorine and hydrogen enables the dark reaction to occur even at 100°, whereas in the absence of sodium this reaction takes place only at 300°.

$$Na_2 \rightarrow Na^{\cdot} + Na^{\cdot},$$
$$Na^{\cdot} + Cl_2 \rightarrow NaCl + Cl^{\cdot},$$
$$Cl^{\cdot} + H_2 \rightarrow HCl + H^{\cdot},$$
$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot}, \text{ etc.}$$

As a result, 1000 HCl molecules are formed for every Na atom which has reacted. The effect of a number of other initiators on the chlorination of the lower alkanes has been investigated. Thus in the presence of tetraethyllead, chlorination of ethane with 95% consumption of the chlorine takes place even at 132°, whereas the thermal chlorination starts[12] only at 280°; the composition of the chlorination products is the same in the two cases.

Tetraethyl-lead is highly effective even at extremely low concentrations in the reactant mixture (~0.002 vol.%). Good results have also been obtained in the chlorination of propane, n-pentane, and other alkanes. That of propane takes place at 136°–140° with more than 95% of the chlorine reacting. Chlorination of liquid n-pentane in the presence of $Pb(C_2H_5)_4$ is quantitative.

The initiating action of $Pb(C_2H_5)_4$ at temperatures below 150° (at which thermal decomposition starts) is explained by the formation not of ethyl radicals

$$Pb(C_2H_5)_4 \rightarrow Pb + 4C_2H_5^{\cdot},$$

but of active chlorine atoms, resulting from the reactions

$$Pb(C_2H_5)_4 + 4Cl_2 \rightarrow PbCl_4 + 4C_2H_5Cl \text{ and } PbCl_4 \rightarrow PbCl_2 + 2Cl^{\cdot}.$$

Lead tetrachloride is unstable even at room temperature, and, in contrast to other metal chlorides, is readily decomposed with the formation of chlorine atoms instead of ions[14].

Tetraphenylethane and azomethane have been used for the dark chlorination of alkanes[12,57], but they are less active than metal alkyls as initiators for the vapour-phase chlorination. Thus in the presence of azomethane at 144°, the chlorination of n-butane uses up 5.5–6% of chlorine, whereas in the absence of azomethane no reaction takes place at this temperature[57].

In the chlorination of liquid alkanes the greatest practical use has been made of various organic peroxides (*e.g.* benzoyl, lauroyl, and phthaloyl peroxides) and azo compounds (*e.g.* azodiisobutyronitrile), added in amounts of 0.01–1% to the alkane. In the presence of these initiators chlorination takes place readily and rapidly at temperatures of about 70°–120°.[58,59]

The use of a solvent which is inert towards chlorine as the reaction medium makes it possible to employ the above initiators for the chlorination of gaseous alkanes as well. Thus ethane can be chlorinated at 65°–70° in CCl_4 containing 1% of azodiisobutyronitrile, benzoyl peroxide, or dimethyl percarbonate, 60% of the ethane being converted into chlorinated derivatives[60].

VI. EFFECT OF SURFACE

The surface of the reaction vessel and of its packing material substantially affects chlorination processes, causing both initiation and termination of chains. Under steady-state conditions the effect of the surface is apparently due to its acquisition of semiconducting properties by forming a firmly adsorbed film of the components of the reaction mixture (adsorption being effected by valency or coordinate bonds)[1,41,61].

The thermal chlorination of 2,2,4-trimethylpentane, 2,3-dimethylbutane, n-pentane, n-hexane, and n-heptane in a Pyrex glass reaction vessel is preceded by an induction period of 30–60 min depending on the alkane[11]. The existence of the induction period has been shown to be associated with the absorption of hydrocarbon radicals by the surface of the vessel. The hydrophobic film which is formed has the composition $\gtrdot Si-O-R$, and is removed by washing the reaction vessel with concentrated alcoholic potash or by oxidation in a current of oxygen at 300°. The maximum rate of chlorination is reached when this film is formed. If the surface is contaminated with highly chlorinated reaction products, for example when the process is prolonged, the rate of chlorination gradually falls, which suggests that the $\gtrdot Si-O-R$ film plays an active part in the catalysis of chain processes[28]. The presence of the semiconducting layer causes the appearance of free valences on the surface, which arise under the influence of thermal motion and possess the properties of a free radical. A chlorine molecule from the gas phase incident on a point of the surface having a free valence V, reacts with the latter

$$Cl_2 + V \rightarrow VCl + Cl^{\cdot}, \quad (I)$$

to yield an active chlorine atom in the reaction zone. As with all free-radical reactions, the activation barrier to such a reaction is low, which explains the ease with which the surface generates free chlorine atoms. The energy of the $V-Cl$ bond is, of course, considerably greater than that of Cl–Cl. Chain termination during chlorination is mainly due to chemisorption of the free chlorine atom. On collision with the active surface, the Cl· is first held by comparatively weak forces, a one-electron bond apparently being formed. From this weakly bound state the Cl· can either escape back into the reaction space or surmount the activation barrier and become firmly chemisorbed by forming the surface compound VCl:

$$V_2 + Cl^{\cdot} \rightarrow VCl + V, \quad (II)$$

where V_2 is an element of surface which can form two free valences by dissociation:

$$V_2 \rightarrow V + V - U \text{ kcal}. \quad (III)$$

The presence of a considerable activation barrier in reaction (II) as compared with (I) is responsible for the change in character of the surface effect with change in temperature. Surface activation of the chain process occurs mainly at comparatively low temperatures, close to those at which chlorination of the alkane starts. At higher temperatures the surface begins to exert a retarding effect on the reaction. The energetic non-uniformity of the surface, which derives from its physical non-uniformity, results in chain initiation and chain termination taking place simultaneously on the surface. At relatively low temperatures, however, the rate of initiation predominates over that of termination, so that an increase in the surface : volume ($S:V$) ratio in this case tends to accelerate the chlorination. With rise in temperature the rate of chain termination on the surface exceeds that of surface initiation. As a result, the surface has the opposite effect: *i.e.* at higher temperatures an increase in the $S:V$ ratio tends to retard the chlorination. Thus Fig. 6 shows that in the thermal chlorination of n-butane the packing (short lengths of glass tubing) accelerates the process[50] up to about 250°. Above this temperature the packing starts to retard chlorination, and at

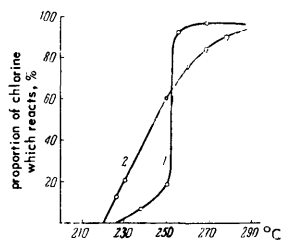


Fig. 6. Temperature variation of proportion of chlorine which reacts in the thermal chlorination of n-butane:
1) without packing; 2) with packing.

300° it no longer has any effect. This is apparently explained by the predominance of bulk chain initiation due to the dissociation of molecular chlorine into free atoms. The activation and inhibition of free-radical chain reactions by the surface undoubtedly depends on the chemical composition of the latter and also on the presence and composition of inclusions. This aspect of the surface effect has unfortunately been little investigated, and existing data are not very accurate because it is difficult to produce surfaces of comparable characteristics. A number of investigations have shown, however, that the type of packing employed has a marked effect both on the reduction in temperature and on the composition of the products. Thus the optimum temperature for the thermal chorination of n-butane is lowered from 300° to 200° in the presence of active aluminium oxide, and to 170° in the presence of silica gel. With a space velocity of ~300 h^{-1} for the process and an n-butane: chlorine molar ratio of 4.5 : 1, the whole of the chlorine is consumed in all cases[50]. The effects of different packings on chlorination processes can be estimated from the activation energy (see Table 5)[50].

TABLE 5. Activation energies for the chlorination of n-butane using different packings.

Packing	Apparent activation energy, cal $mole^{-1}$
No packing	39 000
Pieces of glass tubing	17 000
Active aluminium oxide	14 700
Silica gel	8 200

The use of highly porous packings usually results in an increased yield of di- and poly-chlorides. This is primarily explained by the fact that chlorine and alkyl chlorides are considerably more readily adsorbed than are the lower alkanes, resulting in a more thorough chlorination.

In the chlorination of n-butane on active aluminium oxide and silica gel, 50% of dichlorobutanes are formed, whereas in the purely thermal gas-phase chlorination (at 300° and with the same proportions of the components in the reaction mixture) monochlorobutanes are formed practically exclusively. This effect is most clearly exhibited in the chlorination of methane on activated charcoal, carbon tetrachloride being the main product at both low and high temperatures[62].

Further investigation of the chlorination of alkanes is needed to clarify the laws governing the reaction and its mechanism. This should lead to a better control of the chlorination process and yield new derivatives from natural gas and from petroleum of the greatest value to the national economy.

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SORPTION AND CHROMATOGRAPHY OF MACROMOLECULAR SUBSTANCES

G. V. Samsonov

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I. INTRODUCTION

The considerable successes recently achieved by sorption and chromatographic methods for the separation, isolation, and purification of substances of low molecular weight have given rise to a series of papers on the fractionation of macromolecular compounds using these methods, and also on the application of chromatographic methods to the analysis of polymer mixtures. Advances in sorption and chromatographic methods as applied to polymers have been due on the one hand to the development of a theory and a laboratory technique of chromatography whereby mixtures of very similar substances can be separated, and on the other to the synthesis of specific polymeric sorbents, mainly ion-exchange resins, the structure of which can be controlled during their preparation. The preparation of cross-linked polymeric sorbents, possessing great intramolecular porosity and capable of absorbing large quantities of macromolecular ions, has been especially important in this connection.

Nevertheless, the development of sorption and chromatographic methods for separating and analysing polymers has encountered a number of difficulties which were of no significance in work with substances of low molecular weight. The first important obstacle was the low rate at which sorption equilibrium is established. Although, in the absorption of substances of low molecular weight, decreasing the grain size of the sorbent and creating conditions under which the boundaries of the chromatographic zones were sharpened enabled the spreading of the bands in the sorption column to be successfully overcome, with macromolecular substances it proved considerably more difficult to sharpen the boundaries of the chromatographic bands. A second circumstance impeding the development of sorption methods in this field is the complicated dependence of the sorption capacity on the molecular weight of the absorbed substances. The capacity increases with increasing molecular weight in a series of homologous polymers of comparatively low molecular weight, and decreases with polymers of relatively high molecular weight[1-5]: on the one hand the usual increase in sorption capacity in conformity with Traube's rule, and on the other a decrease due to the fact that large molecules cannot penetrate the pores of the sorbent. This latter phenomenon, of course, can prove useful in a number of cases for the separation of polymers according to their molecular weights, on the molecular sieve principle.

The dependence of the sorption capacity of polymers on the composition of the solvent in contact with the sorbent has been studied with several materials[4,6,7]. Thus more polystyrene is sorbed by activated charcoal from the comparatively "poor" solvent ethyl methyl ketone than from the "better" toluene[7]. Addition of the very "poor" solvent methanol to ethyl methyl ketone improves the sorption of polystyrene[4]. This phenomenon can be compared with the analogous influence of solubility on the sorption capacity of a substance observed earlier by Tiselius[8].

The rate of sorption of polymers is greatly dependent on their molecular weight. A series of investigations by Yurzhenko *et al.*[9,10] has shown that polyisopropylene, polystyrene, and butadiene–styrene rubber of low molecular weight are sorbed on carbon black much more rapidly than are samples of the same polymers having high molecular weights. The sorption of an unfractionated polymer is accompanied by an increase in the intrinsic viscosity of the solution surrounding the sorbent, indicating selective absorption of the low-molecular-weight fraction[9,10]. The low rate of sorption on carbon black of the high-molecular-weight fraction of butadiene–styrene rubber produces the very interesting phenomenon that, after a certain time,