

MORRISON
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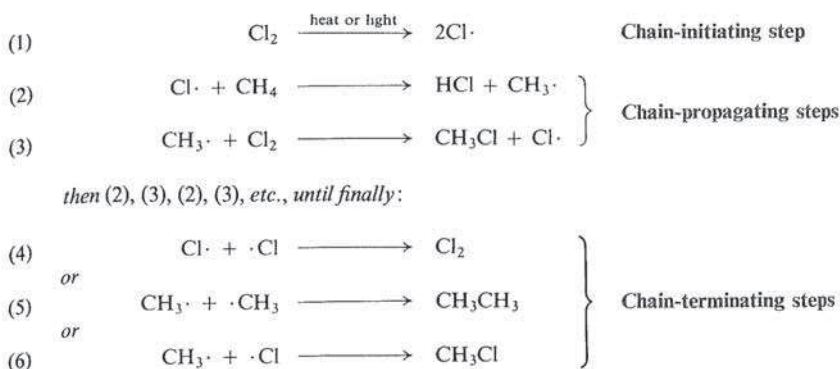
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the next step. While chain reactions may vary widely in their details, they all have certain fundamental characteristics in common.



First in the chain of reactions is a **chain-initiating step**, in which energy is absorbed and a reactive particle generated; in the present reaction it is the cleavage of chlorine into atoms (step 1).

There are one or more **chain-propagating steps**, each of which consumes a reactive particle and generates another; here they are the reaction of chlorine atoms with methane (step 2), and of methyl radicals with chlorine (step 3).

Finally, there are **chain-terminating steps**, in which reactive particles are consumed but not generated; in the chlorination of methane these would involve the union of two of the reactive particles, or the capture of one of them by the walls of the reaction vessel.

Under one set of conditions, about 10 000 molecules of methyl chloride are formed for every quantum (photon) of light absorbed. Each photon cleaves one chlorine molecule to form two chlorine atoms, each of which starts a chain. On the average, each chain consists of 5000 repetitions of the chain-propagating cycle before it is finally stopped.

2.14 Inhibitors

Finally, how does the mechanism of chlorination account for fact (f), that a small amount of oxygen slows down the reaction for a period of time, which depends upon the amount of oxygen, after which the reaction proceeds normally?

Oxygen is believed to react with a methyl radical to form a new free radical:



The $\text{CH}_3\text{OO}\cdot$ radical is much less reactive than the $\text{CH}_3\cdot$ radical, and can do little to continue the chain. By combining with a methyl radical, one oxygen molecule breaks a chain, and thus prevents the formation of thousands of molecules of methyl chloride; this, of course, slows down the reaction tremendously. After all the oxygen molecules present have combined with methyl radicals, the reaction is free to proceed at its normal rate.

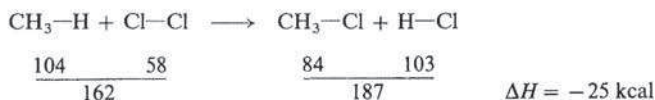
A substance that slows down or stops a reaction even though present in small amount is called an **inhibitor**. The period of time during which inhibition lasts, and after which the reaction proceeds normally, is called the **inhibition period**. Inhibition by a

relatively small amount of an added material is quite characteristic of chain reactions of any type, and is often one of the clues that first leads us to suspect that we are dealing with a chain reaction. It is hard to see how else a few molecules could prevent the reaction of so many. (We shall frequently encounter the use of oxygen to inhibit free-radical reactions.)

2.15 Heat of reaction

In our consideration of the chlorination of methane, we have so far been concerned chiefly with the particles involved—molecules and atoms—and the changes that they undergo. As with any reaction, however, it is important to consider also the energy changes involved, since these changes determine to a large extent how fast the reaction will go, and, in fact, whether it will take place at all.

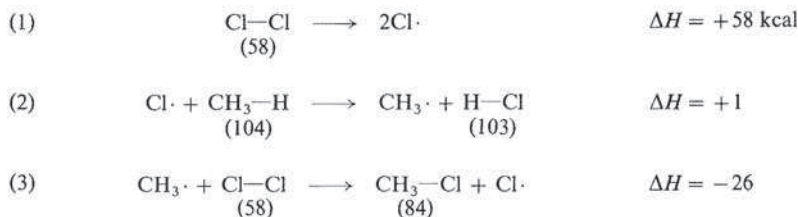
By using the values of homolytic bond dissociation energies given in Table 1.2 (p. 21), we can calculate the energy changes that take place in a great number of reactions. In the conversion of methane into methyl chloride, two bonds are broken, $\text{CH}_3\text{—H}$ and Cl—Cl , consuming $104 + 58$, or a total of 162 kcal/mol. At the same time two new bonds are formed, $\text{CH}_3\text{—Cl}$ and H—Cl , liberating $84 + 103$, or a total of 187 kcal/mol. The result is the liberation of 25 kcal of heat for every mole of methane that is converted into methyl chloride; this is, then, an **exothermic reaction**. (This calculation, we note, does not depend on our knowing the mechanism of the reaction.)



When heat is liberated, the heat content (enthalpy), H , of the molecules themselves must decrease; the change in heat content, ΔH , is therefore given a negative sign. (In the case of an endothermic reaction, where heat is absorbed, the increase in heat content of the molecules is indicated by a positive ΔH .)

Problem 2.1 Calculate ΔH for the corresponding reaction of methane with: (a) bromine, (b) iodine, (c) fluorine.

The value of -25 kcal that we have just calculated is the *net* ΔH for the overall reaction. A more useful picture of the reaction is given by the ΔH values of the individual steps. These are calculated below:



It is clear why this reaction, even though exothermic, occurs only at a high temperature (in the absence of light). The chain-initiating step, without which

SEC. 2.16

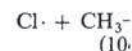
reaction cannot occur only at a high temperature. propagating steps occur readily, but chlorine is the best that can be taken.

Problem 2.2 Calculate ΔH for the reaction of methane with: (a) bromine

We have assumed that the reaction proceeds with difficulty. assumed relations when other information is available and there are many other energy quantities that way to rate of reaction.

2.16 Energy of

To see what happens closely at a specific



This reaction is complicated by the atom and the principles that apply.

Just what must be done and a methane molecule, a hydrogen

Next, to be energy.

Formation of $\text{CH}_3\text{—H}$ bond requires additional energy. Bond-breaking liberates the energy liberated. Experiment has shown that energy must be supplied.

The minimum energy to occur is called the moving particles. If the reaction is fruitless, the original particles one or bring about reaction in 40 is sufficient.