THE MECHANISM OF SOME IMPORTANT ORGANIC REACTIONS

The Dissociation of Carbon Bonds[1]

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The dissociation of carbon bonds is one of the most important reactions in organic chemistry. The cracking process and the scission of sugar are examples which reveal not only its importance in industry, but also in the whole life process itself.

THE SCISSION OF A HOMOPOLAR BINDING

The rupture of carbon bonds is a process of dissociation; a homopolar bond between two carbon atoms is broken and two molecules are formed from one.

A bond is heteropolar if the residues which are connected by it are ions, and homopolar if they are not; in the first case the energy of binding is due to Coulomb attraction, in the second to the resonance energy of two electrons of different spin. The molecules of simple gases such as hydrogen and chlorine and those of the enormous number of organic compounds are held together by homopolar bindings.

In the first paper (32) on the mechanism of heterogeneous catalytic organic reactions we discussed catalytic hydrogenation, a reaction in which the atoms of the hydrogen molecule are attached to a double bond:

$$CH_2{=}CH_2 + H_2 = CH_3{-}CH_3$$

In this case we also have a process of splitting off homopolar bonds; the binding between the two hydrogen atoms and one of the double bonds must be loosened to give ethane as end product.

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[1] This is the second of a series of three papers; for the first see reference 32.

We have seen that the mechanism of this process is quite different with different catalysts and have found that there are two classes of catalysts. The first consists of the higher elements of the alkali group and the elements of the alkaline earths; these elements have large atomic and ionic volumes and small work functions. The second consists of transition elements, e.g., the elements of the iron and platinum group, with small atomic and ionic volumes and relatively large work functions.

With catalysts of the first class hydrogen is activated by forming primarily negative ions:

$$H_2 + 2\bar{e} \rightarrow 2H^- \tag{1}$$

With catalysts of the second class primarily positive ions of hydrogen, especially protons, are formed:

$$H_2 \rightarrow 2H^+ + 2\bar{e} \tag{2}$$

The third possibility, that primarily the hydrogen molecule is split into two atoms without adding or subtracting electrons,

$$H_2 \rightarrow 2H \tag{3}$$

seems not to be effected in catalytic hydrogenation, which occurs in metallic solution. But in the reactions in which carbon bonds are broken, normally uncharged groups or residues are formed as in equation 3.

To investigate reactions of this type, we must first consider thermal dissociations in the gas space, in which wall-effects do not occur. The cracking of hydrocarbons in vessels of quartz or Pyrex glass is a monomolecular and homogeneous reaction, as Pease and Durgan (24) have shown. According to the definition of van't Hoff, in a monomolecular reaction a molecule is split according to the equation:

$$A = B + C$$

First the molecule of the hydrocarbon must take up internal energy in order that the work of dissociation can be done. This is effected by an inelastic impact. The process of dissociation, as for instance the elementary process of the cracking reaction, is therefore divided into three phases: (1) the inelastic impact, (2) the dissociation into two particles, and (3) the subsequent reactions.

In the following, we consider only the last two phases of the process.[2]

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[2] The first phase has been discussed by the author (Ann. Physik [5] **21**, 241–67, 268–73 (1934)).

We begin with the scission of the sugar molecule in dilute aqueous solution, a process which is comparable to a reaction in the gaseous state.

A. The scission of the sugar molecule

A large fraction of enzymatic reactions in the living cell consists of reactions in which homopolar bonds from carbon to carbon or to other atoms are split. In the process of fermentation by the enzymes of yeast, such as zymase, bonds between carbon atoms are broken. The esterases such as lipase, the chlorophyllases, the carbohydrases such as saccharase, maltase, and emulsin loosen the bond between carbon and oxygen. The proteases such as pepsin, trypsin, and papain, the amidases such as histocyme, arginase, and urease, loosen the bond between carbon and nitrogen. In many cases, as in the processes of fermentation and of digestion, for instance, these reactions are not reversible and lead to a diminution of the molecular weight.

Neuberg and his coworkers have found (19) that the enzymatic scission of glucose follows the equation

$$C_6H_{12}O_6 \rightarrow 2CH_3COCHO + 2H_2O \qquad (4)$$

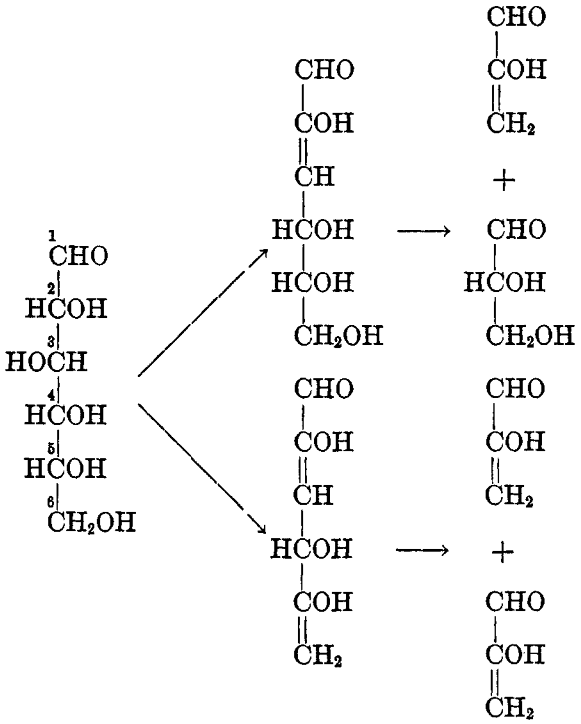
First the glucose is split into two molecules of methylglyoxal, with three carbon atoms in the molecule, and therefore the rupture of carbon bonds takes place in the middle of the carbon chain. The molecule of methylglyoxal is then converted into alcohol and carbon dioxide.

The scission of the molecule of glucose in the organism produces lactic acid, also a compound with three carbon atoms in the molecule:

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH \qquad (5)$$

The conversion of glucose in blood into lactic acid is produced by the leucocytes, which cover the lack in energy for the life process by this scission (1); in carcinomas the production of lactic acid from blood sugar is a typical process of the cancer cells, as Warburg has shown (39, 40); finally the oxidative combustion of the lactic acid produced by glucolysis delivers the energy to the working muscle, as Meyerhof has shown (7).

Neuberg formulates the scission of glucose (23) in the following manner, supposing that first the oxydic bonds are broken and a free aldehyde group is formed, a process called oxycyclodesmotropism by Jacobson.



(6)

This formulation cannot be right. As I have shown (29), the double bond between two carbon atoms strengthens the following single carbon bond and weakens the next following; this alternation of strong and weak single carbon bonds goes through the whole carbon chain with decreasing energy (double bond rule). Examples for this rule are given in table 1. Therefore, counting from the double bond as one, the next single carbon bond[3] 2 is strengthened, the following bond 3 is weakened. Bond 2, beside the double bond, is never broken within wide limits of temperature. In the formulas of Neuberg the double bond lies by the side of the bond to be dissociated; here a rupture is impossible.

The scission of glucose into two parts each with three carbon atoms in the molecule is not only effected by the enzymatic bodies of the yeast and the ferments of the cell, but also by hydroxyl ions. These are also able to split glucose into methylglyoxal, although this homogeneous reaction does not proceed with the same good yield and the same uniformity as the microheterogeneous one that is produced by the enzymes of yeast.

Nef (17) has made a special study of the reaction of hydroxyl ions in

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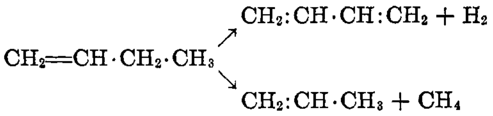
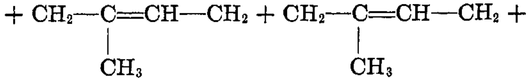
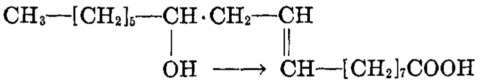
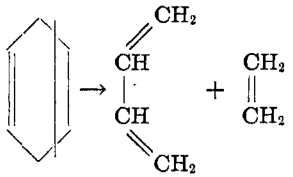
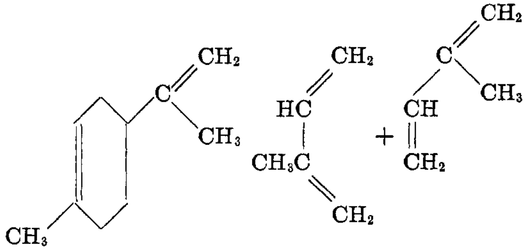
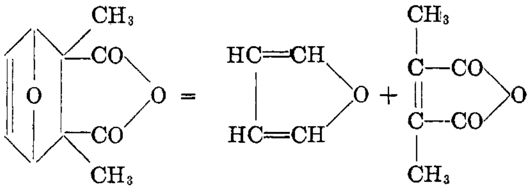
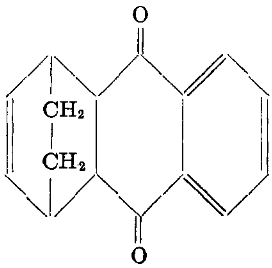
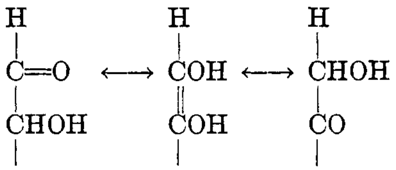
[3] Bond 2 is the bond between the carbon atoms 2 and 3; bond 3 that between carbon atoms 3 and 4, etc.

TABLE 1

Examples for the double bond rule

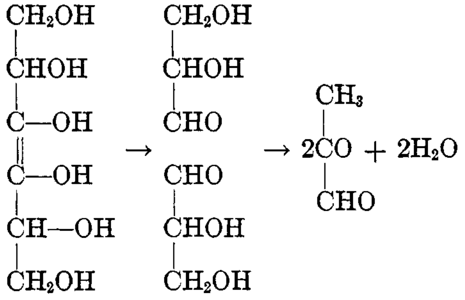
COMPOUND	RESULT	SCISSION RELATIVE TO THE DOUBLE BOND (=1) IN	AUTHOR
α-Butylene .	 $CH_2{=}CH\cdot CH_2\cdot CH_3 \nearrow CH_2{:}CH\cdot CH{:}CH_2 + H_2$ $CH_2{=}CH\cdot CH_2\cdot CH_3 \searrow CH_2{:}CH\cdot CH_3 + CH_4$	3	Calingaert (44)
Natural rubber . . .	 $+\ CH_2-\underset{\underset{CH_3}{\vert}}{C}{=}CH-CH_2+CH_2-\underset{\underset{CH_3}{\vert}}{C}{=}CH-CH_2+$	3	Williams (45)
Ricinoleic acid.	 $CH_3-[CH_2]_5-\underset{\underset{OH}{\vert}}{CH}\cdot CH_2-\underset{\underset{CH-[CH_2]_7COOH}{\Vert}}{CH}\ \longrightarrow$ Heptaldehyde Undecylenic acid	3	Krafft (46)
Tetrahydrobenzene . .		3	Schmidt (47)
Dipentene. .		3	Staudinger (48)
Dehydrated canatharidine.		3	v. Bruchhausen and Bersch (49)
Endoethylene dihydroanthraquinone	 $= C_{14}H_8O_2 + C_2H_4$	3	Diels and Alder (50)

alkaline aqueous solutions and glucose. It is well known that hydroxyl ions isomerize the aldehyde and keto group into enols; e.g., the esters of acetoacetic acid, which consist chiefly of the keto form in liquid state, are enolized by alkali. Therefore, in the hexoses, we get 1,2-dienols from the aldehyde or keto group according to the following scheme:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{CHOH} \\ | \end{array} \longleftrightarrow \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{COH} \\ \| \\ \mathrm{COH} \\ | \end{array} \longleftrightarrow \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CO} \\ | \end{array} \qquad (7)$$

As the 2-ketose can also give a 2,3-dienol, which can be produced by a 3-ketose, it is apparent that the double bond can thus run through the whole sugar molecule. Indeed Nef assumes this sequence of reactions and believes that the 3,4-dienol is the intermediate product of the scission of sugar with formation of glyceric aldehyde, which then easily produces methylglyoxal.



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{C{-}OH} \\ \| \\ \mathrm{C{-}OH} \\ | \\ \mathrm{CH{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array} \rightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHO} \\ \\ \mathrm{CHO} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} \rightarrow 2\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CHO} \end{array} + 2\mathrm{H_2O} \qquad (8)$$

The 1,2-dienols, according to Nef, are broken into chains of five carbon atoms; the 2,3-dienols into chains of four carbon atoms. This explanation seems very improbable. The 3,4-dienol is, according to Nef, the product of a series of changes of the 1,2- and 2,3-dienol; it is not possible to understand why scission would take place only at the end of this series and not at every intermediate stage. A quantitative yield with compounds of three carbon atoms, such as we get in the scission of sugar by enzymes in the process of fermentation, is completely incomprehensible.

The double bond rule gives another explanation, which is more probable. Even the 1,2-dienol, the first product of conversion of glucose, can be broken in the middle because the bond between the carbon atoms 3 and 4 is weakened. Therefore the reaction goes on as follows: the molecule,

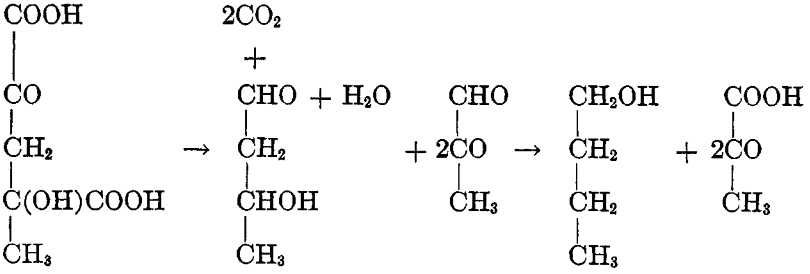
$$\mathrm{HC(OH){-}C(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH_2(OH)} \qquad (9)$$

is broken in the middle to form two molecules of methylglyoxal.

In the process of fermentation without yeast cells, we find as intermediate products three esters of hexose with phosphoric acid, which carry the phosphoric groups at the end of the sugar molecule: 1) the ester of Harden-Young, fructofuranose-1,6-diphosphoric acid (16); 2) the ester of Neuberg, fructofuranose-6-phosphoric acid (18); 3) the ester of Robinson, glucopyranose-6-phosphoric acid (13, 28). As these hexosemono- and diphosphoric acids are fermentable as such with difficulty, it is probable that these intermediate products give rise to other products, in which the splitting of the carbon bond at the middle of the sugar molecule is facilitated. We shall suppose that these other products are the 1,2-dienols mentioned before. According to this thesis the rupture of the carbon chain of the glucose molecule is alike whether enzymes or alkalies are used. The process in both cases leads to the same intermediate products, the 1,2-dienols, in the first case by way of the above esters, in the second case, directly.

According to the double bond rule the location of the rupture must be different in the different dienols of hexoses: the 1,2-dienols will split off in the 3,4-position, the 2,3-dienols in the 4,5-position. In the first case compounds with three, in the second case compounds with four and two carbon atoms in the molecule are formed, and whether the numbers of carbon atoms in the chains are conserved or not depends on the conditions of reaction.

Amylum can be fermented by especial varieties of yeast with the formation of large amounts of butyl alcohol (38). Neuberg and Arinstein assume that this *n*-butyl alcohol is the product of a synthesis from smaller fragments which are formed in the process of fermentation (20). This assumption seems probable at first sight because Buchner and Meisenheimer (2) have found that glycerol, on fermentation with *Bac. butylicus*, gives butyl alcohol, ethyl alcohol, and carbon dioxide. Neuberg and Arinstein assume that the aldol of pyruvic acid, formed from pyruvic acid, is the intermediate product, and formulate the reaction as follows:



$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{C(OH)COOH}\\ |\\ \mathrm{CH_3}\end{array} \rightarrow \begin{array}{l}2\mathrm{CO_2}\\ +\\ \mathrm{CHO}+\mathrm{H_2O}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CHOH}\\ |\\ \mathrm{CH_3}\end{array} \begin{array}{l}\mathrm{CHO}\\ |\\ +\,2\mathrm{CO}\\ |\\ \mathrm{CH_3}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\end{array} \begin{array}{l}\mathrm{COOH}\\ |\\ +\,2\mathrm{CO}\\ |\\ \mathrm{CH_3}\end{array} \tag{10}$$

It is possible that the reaction proceeds thus in the above case, but it is not necessary that the scheme of reaction be the same in the case of amylum. It seems to be much more probable that chains with four carbon atoms are formed directly by the scission of a 2,3-dienol.

There is a process of rupture of carbon bonds in a chain of six carbon atoms which can be interpreted only on the latter basis, namely, the hydrogenating scission of hexitol. I have found (31) that this scission is effected by hydrogenating hexitols with catalysts of the second class (nickel, cobalt, etc.) under pressure (e.g., 300 atmospheres) at a temperature of about 200°C. This is the temperature at which *hydrogenating catalysts* of this class *have dehydrogenating properties.* The scission of sorbitol, mannitol, and dulcitol forms principally 1,2-propylene glycol and isopropyl alcohol, according to the equations:

$$C_6H_{14}O_6 + 3H_2 = 2C_3H_8O_2 + 2H_2O \qquad (11a)$$
$$C_3H_8O_2 + H_2 = C_3H_8O + H_2O \qquad (11b)$$

These reaction products are also obtained if glycerol is hydrogenated under the same reaction conditions. Only a small part of the hexitol is split off to form chains of four and two carbon atoms—2,3-butylene glycol, ethylene glycol, and ethyl alcohol—according to the equations:

$$C_6H_{14}O_6 + 3H_2 = C_4H_{10}O_2 + C_2H_6O_2 + 2H_2O \qquad (12)$$
$$C_2H_6O_2 + H_2 = C_2H_6O + H_2O \qquad (13)$$

2,3-Butylene glycol is also obtained if erythritol is hydrogenated under the same conditions.

It is extremely improbable that in this high pressure hydrogenating process butylene glycol is formed from active fragments of scission, because such active fragments would first be hydrogenated and would then be unable to react together to form larger molecules. Therefore the same may be expected in the case of the sugar scission with enzymes and in alkaline solutions. That the hydroxyl groups at the ends of the molecule are reduced in the hydrogenating process is comprehensible because they are most accessible.

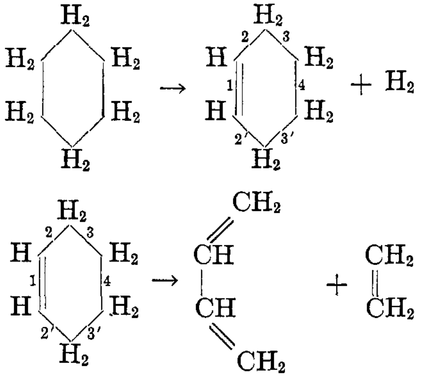
The pentoses react in a similar manner. Fischler and Boettner investigated the scission of arabinose with alkali (5) and obtained a mixture of methylglyoxal and glycolic aldehyde. According to the double bond rule we here also assume formation of a 1,2-dienol as intermediate product of the scission.

B. The cracking process

The scission of the sugar molecule by enzymes and alkali is a process which takes place at ordinary temperature chiefly because the formation of a dienol with its weak bond is effected so easily by a simple isomerization at the room temperature. In the process of splitting hexitols by catalytic hydrogenation a much higher temperature of about 200°C. is needed; this is the temperature at which hydrogenating catalysts show dehydrogenating properties. The first step of the reaction is the formation of a hexose.

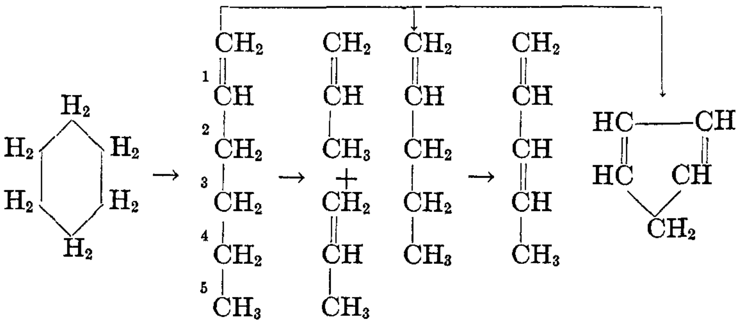
The process of cracking paraffins proceeds according to a similar scheme. Here too the first reaction is the formation of a double bond by the splitting-off of two hydrogen atoms. The location of the double bond is then decisive for the location of rupture. This hypothesis is not the customary one. Heretofore it has been assumed that the breaking of a bond between two carbon atoms is the first step in the cracking reaction.

There is no doubt that by cracking cycloparaffins, such as cyclohexane, the greater part of the molecule is first dehydrogenated to tetrahydrobenzene and then split into two fragments, butadiene and ethylene, as I have shown (29). Therefore the series of reactions with primary dehydrogenation and scission on the weak positions 3 and 3′ is experimentally well founded.



(14)

Only a small proportion of the molecules of cyclohexane is first split into hexylene, probably α-hexylene, by first breaking a bond between two carbon atoms. In this case propylene, amylene, and its conversion products, 1-methylbutadiene and cyclopentadiene, are formed according to the following scheme:



(15)

The mechanism of the rupture is probably the following. The α-hexylene has two weak positions according to the double bond rule: the bonds 3 and 5, of which bond 3 is weaker than bond 5. Therefore compounds with five carbon atoms are formed in smaller amounts than compounds with three carbon atoms.

In cracking aliphatic hydrocarbons, the scission in which chains of three carbon atoms are formed is favored (30) (see table 2). Using the double bond rule, we assume that the first step of the cracking process is the formation of a double bond in position 1,2, by splitting off two hydrogen atoms in the same position, and find:

$$\begin{tikzcd} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \arrow[r] & CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + H_2 \arrow[d] \\ & CH_2{=}CH{-}CH_3 + CH_3{-}CH_2{-}CH_3 \end{tikzcd} \qquad (16)$$

Burk (3) and Rice (25, 27) suggest that the intermediate products of cracking are free radicals. Burk formulates the cracking process of a paraffin by the following equations:

$$C_nH_{2n+2} \rightarrow C_{n_1}H_{2n_1+1} + C_{n_2}P_{2n_2+1} \qquad (17a)$$

$$C_{n_1}H_{2n_1+1} + C_{n_2+1}H_{2n_2+1} \rightarrow \begin{cases} C_{n_1}H_{2n_1+2} + C_{n_2}H_{2n_2} & (17b) \\ C_{n_1}H_{2n_1} + C_{n_2}H_{2n_2+2} & (17c) \end{cases}$$

Indeed, Rice (25, 27) showed that in some cases the cracking process forms the simple free radical CH_3; he demonstrated its existence by using the method of Paneth with mirrors of lead, antimony, and zinc, which vanish in the presence of the free methyl radicals and give volatile metal methyls, $Pb(CH_3)_4$, $Sb(CH_3)_3$, and $Zn(CH_3)_2$. But the temperature used in his experiments was very high (800–1000°C.) and he himself raises the question as to whether this decomposition is the same as that which occurs in the range between 550–650°C. Since the velocity of decomposition follows the Arrhenius equation

$$k = ae^{-\frac{A}{RT}}$$

where $A = 65$ Cal. at the temperatures used, 625°C. and 900°C, this supposition seems to be justified. But it would be possible that the formation of the methyl radical is only a side reaction in both cases and that the main reaction follows another course. It is not possible to determine the proportionate yield of decomposition products and of free radicals from the experimental data in hand. Indeed it seems to be very

TABLE 2

Results of cracking of normal paraffins

HYDROCARBON	TEMPERATURE	*P*	TIME OF HEATING	YIELD OF CRACKING PRODUCTS IN PER CENT	RESULT			AUTHOR
						Scission in	Amount in per cent	
	°C.	*atmosphere*						
n-Butane	600	1	1 min.	ca. 20	$CH_4 + CH_3—CH=CH_2$	1.2	44	Hurd (11)
	700	1		ca. 75	$CH_3CH_3 + CH_2=CH_2$	2.3	46	
					$H_2 + C_4H_8$;		5	
					$2\ H_2 + CH_2=CH—CH=CH_2$		4	
	600	1	19 sec.	ca. 17		1.2	55	Hurd and Spence (12)
	650	1	10 sec.	ca. 42		2.3	40	
						1.2	35	Hague and Wheeler (10)
						2.3	40	
n-Pentane	600	1	ca. 70 sec.	ca. 30	$CH_4 + C_4H_8$	1.2	20	Calingaert (4)
					$CH_2=CH_2 + C_3H_8$	2.3	25	
					$C_2H_6 + CH_3CH=CH_2$ besides H	2.3	55	Norton and Andrews (22)
								Hague and Wheeler (10)
								Hurd (11)
n-Hexane	600	1	1 sec.	ca. 73	$CH_4 + C_5H_{10}$	1.2		Haber (9)
					$C_2H_6 + C_4H_8$	2.3		Hurd (11)
					$C_3H_6 + C_3H_8$ besides H_2, C_4H_6, C_6H_{12}	3.4	Mean reaction	Norton and Andrews (22)
								Hague and Wheeler (10)

improbable that the scission into *free* radicals is the main reaction if hydrocarbons of a higher molecular weight take part in the cracking process.

The time of impact, i.e., the length of time during which the two partners of the impact remain together, has the greatest influence on the course of the reaction. This time depends upon the velocity, the nearest distance d, which the impact partners reach, and this distance depends upon the "softness" of the partners of the impact (33). The "softness" is determined by the exponent n of the potential of repulsion, U_b, in

$$U_b = \frac{k_b}{r^n}$$

as calculated from the second virial coefficient (36). This exponent is small in the case of hydrocarbons which are soft. The longer the time of impact, the less probable is the formation of *free* radicals, which undergo change to form more stable compounds during the time of impact, i.e., of contact.

Senftleben and Hein (35) have investigated the processes of impact in the association of hydrogen atoms to molecules, and have found that this association is the more favored the higher the atomic weight of the inert gas in which the combination takes place.

It is remarkable that Rice observed only the methyl radical, which has the smallest mass. The higher radicals were not found, presumably because they were already transformed in the time of contact of the partners of collision.

Whichever of the various schemes given by Burk (3) and Rice (25) for the cracking process we adopt, the principle is always the same: the first step in the cracking reaction is the breaking of a C—C bond. Rice has justified this explanation by the following consideration (26). The work of dissociation of a C—C bond, Q_2, is smaller by 15 to 20 Cal. than the work of dissociation of a C—H bond, Q_1. If we consider a molecule capable of two types of dissociation having the activation energies E_1 and E_2, respectively, then the relative rates of the two reactions are given by $e^{\frac{E_1-E_2}{2\times T}} : 1$, and we find that for a difference of 10 Cal. at 600° C. the reaction having the activation energy E_1 can be completely neglected at the usual temperatures of the cracking process. Therefore according to Rice the splitting of a C—C bond is much more probable than that of a C—H bond and is the only one possible under the conditions of the cracking process; hereby it is assumed that the values of Q and E are proportional.

Let us consider the two reactions a little more precisely. In breaking a C—C bond two radicals are formed and an energy of about 71 Cal. is needed. These radicals are free, i.e., they have a relatively long life. Rice has found a value of about 0.006 second (27). Therefore we have:

$$CH_3{-}CH_3 \rightarrow 2CH_3 - 71 \text{ Cal.}$$

In breaking two neighboring C—H bonds no hydrogen atoms but a hydrogen molecule is formed; the residual compound has a double bond between two carbon atoms. In this case the balance is quite different. We have

$$CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 - 2D_{C-H} + D_{C=C} - D_{C-C} + D_{H-H}$$

If we take the values for the different energies of dissociation given by Grimm (8) we find

$$CH_3 - CH_3 \rightarrow CH_2{=}CH_2 - 2 \times 92 + 125 - 71 + 100 \text{ Cal.}$$

and this reaction needs only 30 Cal. By using the known values of energy of formation we find that an energy of 43.7 Cal. is needed. Whatever the right value of the different dissociation energies may be, the whole energy needed in the reaction to break a C—H bond is much smaller than that needed to break a C—C bond, if free radicals are formed only in the last case. Therefore the course of the reaction depends upon the conditions of the experiment. Yet in the cracking of aliphatic hydrocarbonsthere can be no doubt that experiments show that the breaking of two C—H bonds and the formation of a double bond is the more frequent reaction.

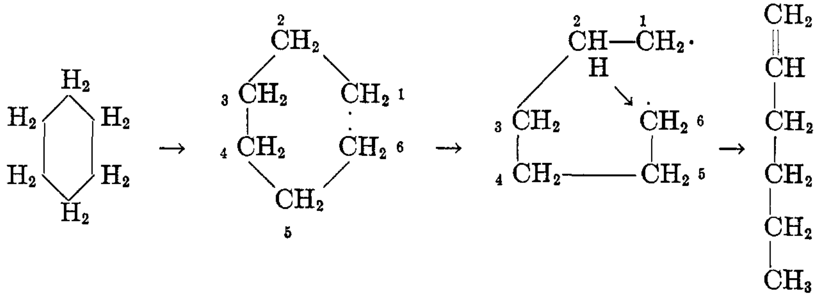
We now repeat the result of our considerations. If two aliphatic hydrocarbons A come into collision and one of them is split, then in the time of contact the latter can first form two radicals with uncoupled valence electrons; and if there are mobile hydrogen atoms these radicals then undergo transformation during the time of contact.

We may interpret the reaction between two molecules of simple hydrocarbons by the equation

$$A^* + A \rightarrow (B^* + C^*)\,A \qquad (18)$$

where A* is a molecule in a state of activation, B* and C* are radicals, and the expression on the right side indicates that the radicals formed are in contact with A. If the time of contact is short enough and the mobility of a radical is great, then it is possible that it escapes before transformation, as we have seen in the case of methyl with its low molecular weight. If there is no possibility of change, then of course radicals with large molecular weight are also stable under favorable conditions. Triphenylmethyl, which has no mobile hydrogen atoms and cannot change without incisive transformations, is quite stable in oxygen-free solutions. Other radicals will undergo transformation to stable molecules in the time of impact (51).

We can now contemplate anew the process of cracking cyclohexane. As we have seen, in most of the molecules two C—H bonds are broken and tetrahydrobenzene is formed, which then gives butadiene and ethylene; but a small part of cyclohexane first gives α-hexylene and a carbon bond is broken according to the scheme:



I II III IV

where the dots in formulas II and III indicate that there are free valences. Thus the hydrogen atom on the carbon atom 2 must travel to the carbon atom 6 to form the relatively stable product, α-hexylene. The probability that such a shift takes place instead of the recombination to cyclohexane is the greater, the closer the hydrogen atoms of carbon atom 2 and carbon atom 6 come together, as is indicated in formula *III*. Finally α-hexylene, with its double bond between atoms 1 and 2, is formed, and then undergoes further transformations in the cracking process as we have seen.

In a normal paraffin chain the binding forces between the carbon atoms of the chain can be assumed to be practically constant. Wierl (42) has measured the distances in Ångström units between the carbon atoms in a chain by his method of electron rays, as follows: ethane, C_2H_6, 1.52 ± 0.1; propane, C_3H_8, 1.52 ± 0.05; butane, C_4H_{10}, 1.52 ± 0.05; pentane, C_5H_{12}, 1.53 ± 0.05; hexane, C_6H_{14}, 1.54 ± 0.05. Investigations with Röntgen-rays have shown that the dimensional increase of the elementary compound per CH_2 group in a series of homologous paraffins is completely constant, the value of this distance being 1.54 A. U. (6, 15, 37). The molecular volume also rises constantly in the series of normal paraffins; the same is true of the molecular refraction, which, according to Clausius-Mosotti, must be regarded as a measure of the volume occupied by the molecule.

We conclude from all these facts that the distances between the carbon atoms adjacent to one another in a paraffin chain are practically equal.

Since these distances are a measure of the binding forces between the carbon atoms, these forces are practically equal. At the ends of the chain we have a CH_3 group instead of a CH_2 group, but this difference probably has no appreciable influence because the distance between the carbon atoms in the molecule of ethane is the same as that in the molecule of propane, within the limit of experimental error.

If now the forces in a carbon chain of a normal paraffin are of the same strength, then the probability that the chain breaks up is the same for any C—C bond. For instance, in the molecule of *n*-pentane, with the bonds 1,2; 2,3; 3,4; and 4,5, the bonds 2,3 and 3,4 are equivalent and 1,2 and 4,5 are also. The probability that scission takes place at 1,2 is $\frac{1}{2}$, and that for 2,3 also $\frac{1}{2}$. In analogous manner we find the probabilities for the other hydrocarbons. But the results of the investigations do not conform to these calculations. Thus for pentane an 80 per cent scission at 2,3 was found, while the calculation gives 50 per cent. For chains of six carbon atoms the calculation gives a probability of 20 per cent at 3,4, whereas *n*-hexane gives more than 50 per cent; the scission of the sugar molecule and the hydrogenating scission of a normal hexitol take place with a yield of about 100 per cent at 3,4. Table 2 illustrates these relations.

Therefore the hypothesis that the first step in cracking consists of the scission of a C—C bond cannot be right. We conclude that the first step is in most cases the scission of two C—H bonds and that the double bond formed orients the place of scission according to the double bond rule.

If we suppose that the hydrogen atoms at the end of the chain are the most reactive because the end is most exposed to impacts, then the formation of a double bond is most probable at 1,2, and the C—C bond at 3,4 is weak according to the double bond rule; here the scission takes place. Indeed *n*-hexane is broken off chiefly at 3,4. Therefore the process of scission of sugar, the hydrogenation of hexitols under pressure, and the cracking process are governed by the double bond rule. Scission takes place in position 3, counting from the double bond as 1.

But according to the double bond rule, bond 5 is also weak, although less weak than 3. How is it possible that scission of sugar with yeast takes place only in position 3? Obviously this is a question of temperature. Let us suppose that the difference of the binding energy between the bonds 5 and 3 corresponds to an activation energy of about 6 Cal., which is probably nearly the right value. The proportion of velocities as between the two splitting reactions at 20°C. would be $e^{\frac{6000}{2 \times 293}}:1 = 28{,}200:1$. This means that the scission at 5 would be negligible because the velocity is 28,200 times smaller. If the difference were 5 Cal., the proportion would be 4,450:1. The proportion would decrease perceptibly only at higher temperatures.

Some observations indicate that scission at 5 takes place at higher temperature. We have seen that in the cracking of cyclohexane a part of the molecules form α-hexylene, which gives principally propylene and in smaller amounts methylbutadiene and cyclopentadiene, two compounds with five carbon atoms. The proportion of chains or rings with three and five carbon atoms amounts to 30:1 at 710°C., and 11:1 at 755°C., if the cyclohexane remains in the contact chamber for ten seconds. The difference Δ of the activation energy value in positions 5 and 3, is therefore found to be 6.7 Cal. and 4.9 Cal., respectively, with an average of 5.8.

A quite analogous case is that of cracking *n*-hexane, a reaction which Haber (9), Hurd and Spence (12), Norton and Andrews (22), Hague and Wheeler (10) have investigated. They found propylene as the main reaction product besides small quantities of amylene. Obviously at first α-hexylene is formed by dehydrogenation, which then is split principally at position 3, in small amounts at position 5.

But some phenomena observed in the scission of sugar also indicate that scission at position 5 takes place in small amounts, as the theory requires. The presence of *n*-amyl alcohol in fusel oil, which Neuberg and Nord (11) established, finds its simplest explanation in the supposition that bond 5 is split off. The observation of Weinland, that in the action of the ferment of ascaride worms on the carbohydrates *n*-valeric acid is formed, is also interpreted most easily in the same manner.

If rupture of a 1,2-dienol or of a monoölefin has taken place at position 5 instead of at 3, the nascent product is unstable so long as it bears the double bond at 1. It still has a weak position at 3; only if a stable configuration is formed by an atomic displacement is the existence of the chain with five carbon atoms secured. In the process of cracking hexamethylene, methylbutadiene and cyclopentadiene are the stable products with five carbon atoms.

It would therefore be possible that the quantity of substances composed of five carbon atom chains, which is formed immediately after the scission, is larger than the quantity which is experimentally weighed, and that therefore the calculated difference of about 6 Cal. for the difference of the activation energy of the process of dissociation of the bonds 5 and 3 is too high. But clearly 5 Cal. is approximately the minimal value. A diminution to 3 Cal. would give a proportion of the velocities of scission of 167:1, and it is very improbable that an amount of scission at bond 5 of 1/167 would escape notice in such a carefully investigated process as fermentation.

The evidence of scission of the carbon bonds at 3 and 5 relative to the carbon double bond at 1 is of essential importance for the theory of the mechanism of splitting carbon bonds. Measured from center to center of a bond, the distance between the bond 3 and the double bond is about 2.5 A. U., the distance of the bond 5 is about 5 A. U. This distance is so large that normal atomic forces of simple bonds do not play a part, because their influence does not go much over 2 A. U. (34). It will be the theme of later experimental investigations to solve these important questions.

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