THE MECHANISM OF STARCH-IODINE REACTION

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(Received October 17, 1957)

III. The supposed structure of iodine-amylose

Let us suppose that the helices were originally present. Iodine is successively added to the system. The temperature is kept constant. The iodine successively added is partially bound, however, it partially remains free as seen from the amperogram. In this state the concentration of free iodine is in equilibrium. After having attained a certain concentration, this equilibrium remains on a constant level and any additional amount of iodine is bound. This can be realized in the following way: the iodine molecule penetrates the interior of the helices and is there retained. The structure of the exterior shell of the iodine molecules is represented by the following scheme :J:J:

Consequently, we have to deal with a stable noble-gas configuration. If the iodine molecule dissociates, one electron might be absorbed and this noble-gas configuration is again obtained (in which case an anion is generated), or 7 electrons are liberated and this behaves as a cation. The space-structure of an iodine molecule can be expressed by 2 heptagonal bodies having one common angle, each angle representing one electron which might be turned over to the hydroxyls. An iodine molecule therefore possesses 12 electrons which are turned over to hydroxyls, thus through hydrogen bonds generating a stable complex. The following questions might arise:

A) Is the pattern of the iodine molecule correct? Is iodine suitable to form this kind of compounds?

B) What evidence given of the formation of a complex? Are there any energetic evidences of this?

C) To which hydroxyls is iodine bound?

Answer to question No. 1.: iodine compounds of this type are known, e. g.: JF_7, HJO_4, etc. The pattern is thus correct.

* The I and II Part of this work were published in the Periodica Polytechnica *1* (1957) No. 2. and 3., respectively.

The following facts, to be dealt with later on, indicate the formation of complexes: the hydrocarbon-like solution, a supposition of Freuderberg, is out of question, because both the value of the maximum of absorption and the one of molecular extinction greatly diverge from it. The blue colour reaction gives evidence of a very thorough rearrangement of the electron shell [6].

A main-valence bond does not seem to be likely either, as iodine might be segregated from iodine-amylose with any agent suitable to react with it. On the effect of alcohol, which under actual circumstances does not react chemically, the amount of bound iodine equally decreases. The iodide ions themselves are able to replace iodine also in the helix [15].

The most emphatic evidence for the existence of hydrogen bond complexes is the following: the energy of main-valence bond of hydrogen is somewhere about 80 Kcal/mol. The energy of an H—J bond amounts to 71,4 Kcal/mol [17]. The energy of the hydrogen bond is between 2 and 8 Kcal/mol [18]. The results of calorimetric measurements were registered by GILBERT and MARRIOTT [13] with 11,2 Kcal/mol, by DUBE [14], with 19,6 Kcal/mol for the binding of 1 mol of J_2 respectively.

The reaction heat figured from the temperature function of equilibrium J_2 concentration by means of the equation of Clausius-Clapeyron amounts, according to our tests, to 17,2 Kcal [27]. Thus relating to 1 mol of hydroxyl about 1,43 Kcal are liberated. This can be considered as evidence of the hydrogen bond.

The answer to the third question can readily be given. In the amylose molecule on one glucose there are 3 free hydroxyls: one primary and two secondary ones. The position of the two secondary hydroxyls is trans. As amylose of "V" type configuration can bind as little as 26% of J_2, and so only 2/3-s of all hydroxyls come into complex bonds. It might be assumed that the unbound 1/3 consists of primary hydroxyls, which form with water molecules the most stable hydrogen bonds. The two secondary hydroxyls being in trans-position are able to bind. This is not a mere supposition, but an experimentally proved fact.

If we treat starch with a 40% formaldehyde solution, the colouring capacity of J_2 successively disappears. The colour turns from blue to violet, hence to red and eventually into yellow. This effect is so near to that, which can be observed in the case of acidic or enzymic decomposition that former authors believed formaldehyde to produce a hydrolytic formation of dextrin. MAGGI [19] stated, however, that the reaction goes hand in hand with an increase of viscosity, and that the specific rotatory power does not decrease proportionally to the intensity of colour. The end product does not reduce the Fehling solution. SAMEC and MEYER [19] stated that in spite of the ceasing of the J_2 reaction, the degree of polimerization does not decrease. They observed that the product attains maximum viscosity by the extinction of J_2 colouring.

Therefore, it is so far certain that the points of the iodine bonds which are evidently the hydroxyls, were occupied by formaldehyde. It remains an open question how this occurs, and which are the hydroxyls in question.

JACOBI [19] has pointed out that starch of the original colouring capacity might be regenerated from the derivative containing formaldehyde and showing no colour reaction with J_2, by extracting formaldehyde with ammonium acetate (in which case hexamethylene-tetramine is formed). In the case of mild reaction conditions, if the formaldehyde treatment is performed, exclusively at room-temperature, for a not excessively long time, the blue colour can be regained even by an effect of a simple water dilution. This is an evident proof that the

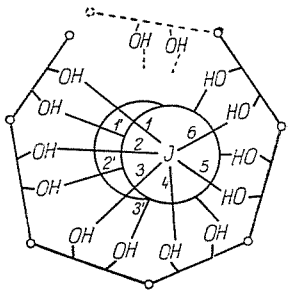

Fig. 1. Space pattern of one period of the iodine-amylose complex. The iodine molecule inserts itself into the interior of the helix

formaldehyde molecules reacted with the active, iodine-binding hydroxyls form hydrogen bonds.

MEYER and a little later WAGNER and PACSU [28] studied the influence of formaldehyde on cellulose. As these hydroxyls of the amylose molecules do not differ from the corresponding hydroxyls of a cellulose molecules, the results obtained in connection to cellulose, can be safely applied to amylose, too.

The above-mentioned authors have stated that formaldehyde only associates with secondary hydroxyls, and does not with primary ones. The methylene bridges are formed between the 2, 3, respectively at the 2, 2 hydroxyls of the different cellulose molecules.

In view of this fact, we can take it for granted that the two secondary hydroxyls are involved in the binding of iodine.

It may be assumed that the glucopyranoside ring is oriented with its edge carrying transhydroxyls towards the iodine molecule, and two hydroxyls of the very same pyrane-ring are bound to different atoms of the iodine molecule. Different hydroxyls of the same pyrane-ring are bound to points marked with the same numbers (see Fig. 1).

Further investigations into the origin of iodine complexes, the following questions arise: why is free iodine present in the solution and on what does the concentration depend.

The concentration of free iodine is influenced by temperature and by the length of the helix. With increasing KJ concentration, iodide ions also intrude into the chain, — as SOZABURO ONO and his co-workers [15] have already pointed out — thus reducing the amount of iodine liable to bounding. In the amperometric titration the KJ concentration is generally low enough and can also be kept at constant level, so that it should not interfere at all.

The role of temperature is more interesting. With rising temperature the free iodine concentration vehemently rises (see part II). In the case of a saturated helix, in view of the structure (to be dealt with later on) only the iodine occupying the ends is liable again to dissociate, and to leave the helix. The iodine molecules surrounded on both sides by iodine molecules within the helix can hardly leave their places, on the contrary, the iodine molecules in the end-positions are liable to do so. The hydrogen bonds not exclusively formed between water and hydroxyls, but those formed between iodine and hydroxyls break down, too, and would continuously re-generate. While the system of pyrane-rings practically "covers tight" the iodine molecules in the centre, iodine molecules at the end position, behave quite differently. The helices do not consist of just the right amount of members that would render it possible for each glucose to be the member of a completed ring, i. e. the degree of polymerization is not a whole multiple member of 6, and even if such would be the case, the iodine molecules are not distributed with perfect regularity, so that some members are deprived of the possibility to bind iodine. These members do not firmly hold their position at the ends of the helices, so that some molecules are being incessantly — so to say — "torn off" from the molecules in the extreme position. This "tearing off" effect is a linear function of temperature increase. The summarized dipole moment yealds a stronger cohesion between the single rings of helices composed of amylose-chains of a considerable length, thus an increase in the binding power of iodine, too. Hydrogen bonds formed by hydroxyls are of the same strength, without respect to the place occupied by them, however, iodine molecules are retained within the helices not only by hydrogen bonds, but by the summarizing dipole moment of iodine molecules, too. Consequently, iodine is more easily liberated from shorter helices.

Dynamic equilibrium rapidly becomes displaced with the rising of the temperature, consequently, the concentration of free iodine also increases. At about 0 C° the concentration of free iodine is naught, too. The reaction is perfectly reversible. As it has previously been pointed out, the concentration of free iodine also depends on the length of the helix and on the degree of polymerization. RUNDLE [7] first stressed that fractions of higher degree of polymerization take up iodine at lower potentials (where the concentration of

free iodine is lower). This was also observed by us, while we performed amperometric titrations. This causes the lack of a sharp break point. In case of hydrolyzed fractions this is also proved by experimental data (see part II, figure No. 7). The explanation is simple : lower degree of polymerization means that there are more helix ends, i. e. more iodine molecules are in a terminal position. Performing titration of a fraction of a lower degree of polymerization at lower temperature, identical iodine concentration can be maintained. This also explains why the colour of dextrins of a lower polymerization grade is not of the original blue ; as dextrins are able to form only few windings, iodine molecules are less firmly bound, which is due to a smaller dipole moment. As was previously pointed out [20, 13) blue colouring needs a polymerization degree of about 30—35.

From here we should revert to the equation of Meyer-Bernfeld. Equilibrium cannot be macroscopically represented because the helices are not simultaneously filled up but one after the other. This has also been experimentally proved by RUNDLE, but it can also be concluded from above facts, if we take into consideration that amylose is strongly heterodispersed and the dispersion corresponding to the degree of polymerization, is most probably continuous. Thus, the equilibrium always relates to a single helix, or more correctly, to a couple of helices, and to the free iodine concentration. The remainder of the — generally shorter — helices, which are just then not under saturation, from the point of view of the equilibrium, are without importance. Thus, the free iodine concentration exclusively keeps equilibrium with the iodine molecules located at the ends of polyiodine chains, consequently, equilibrium depends upon the degree of polymerization and the actual temperature.

Thereafter we have to revert to the question of the structure of iodine saturated helices. As before mentioned, BEAR [21] pointed out that the number of members is strictly determined by the helical rings. As the J_2 sorption of the amylose type "V" is of about 26%, it might be concluded that one molecule corresponds to 6 glucose units. One molecule of iodine can form bindings with 12 hydroxyls. According to the total-isotherm of starch, the extreme value of the adsorption is of 30—40%, too, though — similarly to amylose, and in correspondence to its amylose content — it can only bind about 4—5% iodine. As there is no difference between the strength of hydrogen bonds formed in the two different sections, explanation can only be sought in the space structure.

Amylose binds iodine in the interior of the amylose helix, so that to the strength of the hydrogen bonds the summarized dipole moment should be added, thus discriminating it from the iodine bound to amylopectin merely by means of adsorption. The number of members of a polyiodine chain — forming in the axis of an amylose helix is, in an ideal case, one sixth of the glucose molecules present in the amylose helix. This corresponds to 26,2% of iodine referred to amylose.

This extreme limit can never be attained. It could be approached in two cases: in a dry state, when amylose type "V" binds 26% of iodine vapours, or, if the concentration of the iodine ions are naught, in which case the composition of the formed complex corresponds to six glucoses/1 J_2. Performing titrations, both amperometrically and potentiometrically, the usual measuring solutions of iodine have been used, containing some KJ, too. As has been pointed out by SOZABURO ONO [15] iodide ions are built into the helices, occupy the places of iodine, and the polyiodine chain is divided into several parts. As has previously been mentioned, the glucose units at the ends of amylose helices "hang" free, are "odd". If the polyiodine chain is divided by iodide ions into sections, the number of such "odd" members become considerable. The fact that the 26% taken as an ideal limit generally cannot be attained, this is not due, first of all, to the fact that the iodide ions built in are occupying the places of iodine, but mainly to the fact that the number of iodine molecules this way expelled is greatly outdone by the number of those iodine molecules which are not bound by the "odd" members at the chain ends.

There are also a considerable number of places, which do not bind iodine, because the number of rings between two iodide ions is small, consequently, no stable polyiodine chain with a sufficiently large dipole moment can form.

The glucose units belonging to the afore-said three groups (filled up with iodides, "odds" and sections consisting of less than 30—35 glucose units surrounded by iodide ions) therefore constituting no polyiodine chain and do not bind iodine, as amylose does. The secondary transhydroxyls of these glucose units do not as yet form complexes. Complex forming won't begin but when the helix is filled up, and iodine-excess begins to be present. As iodine in this case is not fixed but by a hydrogen bond-like adsorptive bond and the "mechanical stability", characteristic for iodine within the helix, stability that substantially is due to the summarized dipole moment is missed. The co-operation of three different helices is necessary to create a bond and the forming complex evidently remains very unstable. Consequently, we have to deal here with a typical adsorption depending on the total amount of iodine added, with an always increasing equilibrium concentration of free iodine. The adsorption section of the isotherm cannot begin but after all the places to be occupied in the helices are being taken up by iodine molecules. As a matter of fact, this is described by Freundlichs' isotherm equation. The total-isotherm that comprises both sections of the sorption, consists of two distinct portions. The first section is nearly perpendicular, and this corresponds to the horizontal section of the amperogram. Thus, the equilibrium concentration of iodine is here constant, with no respect to the amount of iodine already bound. The second section corresponds to Freundlichs' equation, with the exception that it tends towards a limit value. It should be pointed out that, plotting the adsorption section of the amperogram, the constant speed of the mixer is essential. This can easily be understood.

The helices associated with the iodine molecules constitute fairly large, ramified aggregates which are highly sensitive to mechanical influences and easily dismember. The side chains of amylopectin molecules are substantially unstable, are liable to form helices of but one or two windings around the iodine molecule. These helices are readily dismembered. This is very clearly shown by the differences existing between the isotherms, according to their way of plotting. The equilibrium iodine concentration is, in the case of stirring, much greater if the mixer is in motion at the adsorption section. This difference is much greater

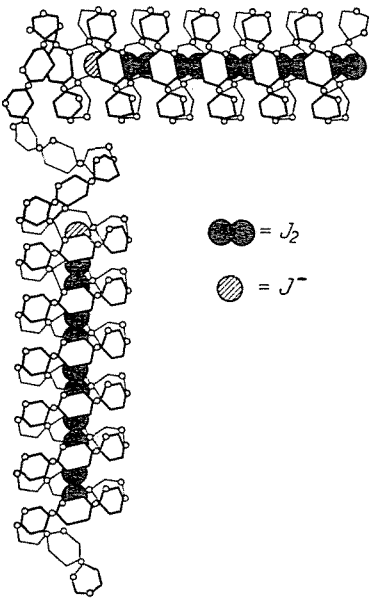

Fig. 2. Structure of the amylose-J_2 complex in the presence of J^- ions

in the case of amylose than in the case of amylopectin, because the aggregates contain more saturated helices. In the neighbourhood of the extreme adsorption value a space lattice structure starts to form. Iodine is trifunctional, while iodine-amylose is polyfunctional. The viscosimetric tests dealt with in part II give perfect evidence to the existence of a lattice structure.

Leaving the question of the origine of helices open for the time being, let us examine the structure of iodine-saturated helix.

The following scheme seems to be the best for representing the structure of iodine-amylose : six glucose units wind themselves, with their edges carrying transhydroxyls around one iodine molecule, and can form with the latter 12 hydrogen bonds. This scheme of a single helix would therefore be the following (Fig. 2).

The rings are not two-dimensional, but have also a substantial lateral extension, in order to preserve the 109° angle of C—O—C bonds from any

substantial deformation. As already mentioned, the glucopyranoside rings are turned towards the iodine molecule with their edges carrying transhydroxyls. With one of the hydroxyls directed in one direction, they are bound to one atom of iodine and with an other hydroxyl turned into the opposite direction to another iodine atom (see Fig. 1).

If four hydrogen bonds of the iodine molecule outside of the helix, i. e. of a molecule already adsorptively bound, disrupts, the iodine results already become detached from the helix, while iodine within the helix does not leave it, even if all the bonds are disruptured, first, because it is surrounded on all sides, and on the other hand, because the summarized dipole moment keeps it in its place. This may be considered as a "mechanical stability".

We must revert to the phenomenon that adding amylase to a starch solution containing enough iodine to saturate the amylose, amylopectin will be affected while amylose, forming a helical complex, will not [6].

The presence of iodine cannot be the only reason of this inhibition, as besides the amylose-iodine complex free iodine is also present, and amylopectin, notwithstanding, will be effected. Let us examine what might be — besides iodine content — the difference between the amylose-iodine complex and the native amylose helix.

a) The dimensions of the helix changed at the effect of iodine, as contraction took place.

b) The secondary transhydroxyls formed bonds.

It seems the most likely that the absence of free secondary hydroxyls causes the lack of enzyme reactions.

Summing up: instead of helices containing 6—8 glucose units per winding, helices containing exactly 6 glucose units are the most likely to be present, though not every coil binds iodine.

Some members of the chain become excluded from binding iodine for the following reasons:

a) Iodide ions occupy the place of iodine.

b) The "odd" members on the chain-ends do not bind.

c) Some, not more than 5 windings are caught between two iodide ions, such windings are not liable to bind iodine firmly. The originally continuous helix deforms to a certain extent. The binding of the iodine molecules is effected by hydrogen bonds. Hydrogen bonds are formed between iodine molecules and secondary hydroxyls. In these helices the glucopyranoside rings are oriented with their edges carrying transhydroxyls towards the iodine molecules, i. e. towards the interior of the coil.

In this way, the second problem dealing with the mechanism of the iodine binding of amylose, seems to be solved.

IV. The structure of the dissolved amylose molecules

Let us revert to the first question that remained to be elucidated. Are there any ready helices before a complex forming agent has been added?

When examining this question, we can start out from 7 various empirical facts.

1. The question concerning the forming of Schardinger dextrins has been already examined in the introduction.

It can hardly be believed that amylose gives a helical form to the straight (the linear) amylose chain, therefore there are only two possibilities : either the forming of Schardinger dextrins do not prove the helical structure — (what should explain in this case the forming of cyclo-amyloses of 6, 7 and 8 members?) or that the helices are present from the beginning. In this case, the theory of instantaneous helix forming is not acceptable.

2. FRENKELS' melting experiment [6]. This has been dealt with in the introduction (part I), too, and it has been pointed out that such experiments do not give evidence of instantaneous helices forming.

3. According to RUNDLE's saturation test [7], the helices are filled up, one after the other. This might partly be explained by the fact that amylose is heterodisperse and the longer coils take up iodine at a lower concentration of free iodine than the shorter ones. It can also be explained by the fact that each helix, first the longest one the dipole moment of which is the largest, becomes — after having taken up the first iodine molecule — activated for the reception of the very next iodine molecule. The mechanism of activization is imaginary in two ways : either no helix was present, and the winding up of the linear molecule had just started, or one of the periods of a helix of some different structure became, through the reception of iodine a six member helix. In this case, the neighbouring two periods are compelled to deform, a further iodine molecule can insert itself, and the dipole moment already summarizes with the one of the iodine molecule bounds.

4. FOSTER-LEPOW's experiment [22]. Amylose dissolved in a mixture of glycerol and ethylenediamine has a viscosity which is substantially lower then that of albumens of the same molecular size. The molecules do not even in a stream substantially orient themselves. At any rate, this gives evidence to the fact that the space structure is in solution, just linear to the solution. If the linear molecules will be fully desoriented, and they occur without any system, coiled and tangled up as is to be expected from a molecule of considerable polimerization degree, i. e. at a substantial length, it can be expected that the binding of iodine does not instantaneously occur, at least at a temperature in the neighbourhood of 0° C. We have carried out amperometric titrations at this temperature range and have stated that the velocity of isopotential iodine sorption is nearly identical with that measured at 25° C. The impossibility

of amylose being present in a tended state in the solution is also proved by the following test: SENTI and VITNAUER [23] have saponified, or brought to reaction with acid, some oriented amylose triacetate and alkali amylose films, which gave well-defined roentgenograms. The regenerated product had readily lost its orientation on the effect of water, the chains had — so to say — "shrunk". The tended chains were therefore trying to assume an other structure, thus the tended amylose molecule behaved just as a tended spring. It is evident that the valence-angle of the C—O—C bond has something to do with the structure developing, which will hardly become desoriented to its full extent.

Therefore, it is quite sure that the amylose molecule in solution has not a tended linear structure nor does it represent an unsystematically tangled ball. A helix-like structure seems to be the most likely, from which the transit to the well-known helical coil is easily performed. We can assume the existence of a true helical form, not, however, in a linear configuration, but irregularly bent. This explains on the one hand that iodine sorption occurs even at a low temperature with substantial velocity and gives, on the other hand, chance for some kind of orientation on streaming. Namely, such a coil still remains rod-shaped. The sizes of an amylose chain of a degree of polymerization of 200 are approximately the following: diameter: about 13,7 Å, length: about 200 Å. Such a structure can also be considered on the basis of LANSKY's et al. [2] observations.

According to these observations, the amylopectin molecules partly dissociated on the effect of a strong mechanical mixer, if starch was treated by some desintegrator, while amylose did not. In their view, this is due to the fact that amylose is liable to orientation.

5. To discern the question, how the structure of the molecule changes, when adding iodine to an amylose solution, the following test was performed: the viscosity of solutions in which amylose concentration had been constantly kept, and only the iodine concentration was increasing, was measured. The results of these tests are shown on figure No. 10 in part II. The breaking point of the curve corresponds to that of the limit of isopotential iodinesorption. From this curve, the rather surprising fact can be concluded that viscosity does not change as long as iodine is taken up by the interior of the amylose helices. If thread-like, long molecules should wind into coils, the viscosity would substantially change. However, as viscosity does not change at all, the iodine sorption cannot cause but insignificant changes in the form of the molecules.

Taking the structure of the iodine containing amylose helices as proved, we must accept the view that helices were also present in the solution, the structure being similar to the structure of helices supposed to exist, according to the former chapter.

The second section of the viscosity curve corresponds to that very state in which iodine is bound by the external part of the helices, and consequently

a space lattice structure is realized. The increase of viscosity is so intensive that the solutions beyond the breaking point within a few hours gains the rigidity of a tixotropical gel.

6. HUSEMANN's acetyl-amylose test [24]. Measuring the viscosity of chloroform and acetone solution of acetyl-amylose, HUSEMANN stated that the viscosity very substantially increases in the function of the acetyl content. It is evident that a certain breaking down takes place during acetylization. What is the reason that viscosity does not decrease?

This is to elucidate that HUSEMANN acetylized an amylose of a known characteristic viscosity. Acetyl amylose was re-saponified and the characteristic viscosity again measured. The very surprising result obtained was that viscosity rose from 0,119 to 0,191. This cannot be explained but by the

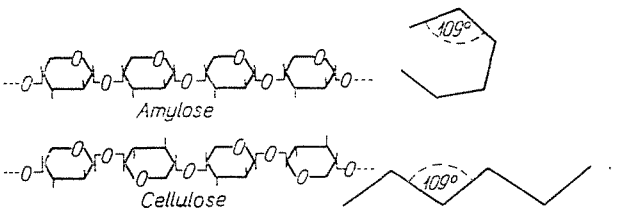

Fig. 3. The difference between the structure of amylose and of iodine (i. e. amylose chains always bend in the same direction, and so, a helix is formed)

fact that, in spite of the intermediate breaking down, the length of the chain molecule had greatly increased. Such a phenomenon cannot be explained but by the assumption that the molecule, that was not originally linear, became linear during the acetylization and the subsequent hydrolysis it has been — so to say — "stretched".

7. The orientation of the stretched amylose films. The chains of amylose and its derivatives show an oriented structure, only in a stretched state, while cellulose also does it without stretching. The valence-angles of the C—O—C bonds of amylose are always directed in the same direction and are additioned. In the case of cellulose the valence-angles compensate each other, thus the molecule is linear (see Fig. 3). This simplified scheme represents the rings — just as HAWORTH-BÖESEKEN's perspectivical sugar formula — as having a flat form while in reality these hexa-rings are not flat. This neglect is not, however, substantial, in view of the fact, that the appearance of the valence-direction of the C atom 1 and 4 are not at all influenced on the projected scheme [25].

As the secondary trans-hydroxyls of the cellulose molecules lay in various directions, they are unable to bind iodine, the single molecule chains are, however, liable to unite through hydrogen bonds to strong fibres. If, however, the bond in some way would become of at least 20—30 glucose units of type, even cellulose would become colourized by iodine. This fact is a further evidence that

the normal structure of amylose cannot be a linear one. Such a structure is only possible in stretched films. Due to the stretching of the valence-angles, the linear structure is richer in energy as against the helical structure. On the other hand, empty helices are unstable and the valence angle of 109° can be deformed without distorsion, on condition that it remains substantially helical. The above statement relating to the energy content of the various forms of amylose, does not contradict the opinion that the helical structure producing a "V" roentgenogram assumes, while retrograding, a lower level of energy. The reason of this is that the levels of energy of various forms of amylose have the following sequency :

a) The highest level of energy is represented by a fully stretched chain.

b) An intermedier level of energy is represented by a perfectly regular helical structure.

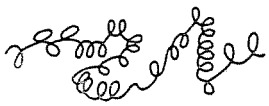

Fig 4. The structure of the deformed helix in a solved state

c) The lowest level of energy is represented by the structure shown on Fig. 4. The disoriented rings reorient under the influence of iodine molecules, forming complexes, without substantially changing the energy content of the molecule, as rotation only occurs around the C—O—C bonds. The rings have six members. In the case of complex formers of a greater size of molecules, e. g. in the case of tertier alcohols, the ring has a larger number of members [21].

Although the afore-said, actually relates only to amylose molecules in solution, it may be imagined, that in granules deformed helices are oriented, too.

Summing up the results of the experiments :

In solutions (probably also in granules) strongly deformed helices occur. The deformation, however, only influences the position of the windings, however, by no means the valence angles of the C—O—C bond. Such coils correspond to the state of the lowest level of energy. Linear forms only occur if amylose films stretched with considerable intake of energy, and to a greater extent in the solution of acetylized amylose.

With the above tests described, the same explanation can also be given to the first question.

Summary

The purpose of our experiments were to elucidate the structure of the dissolved amylose molecules and iodine-amylose produced from it.

According to congruent results of various experiments, the amylose molecule dissolved in water cannot be linear, and should have a structure similar to some helix.

In the complex formed with iodine, iodine is bound by hydrogen bonds. Evidence is given by the value of the reaction heat (17,2 Kcal/mol J_2 equal to 1,43 Kcal/mol hydroxyl). The hydrogen bond forms between iodine molecules and secondary trans-hydroxyls, in such way that the glucopyranoside rings turn with their edges carrying trans-hydroxyls towards the iodine molecules, i. e. towards the interior of the coil. The poly-iodine chains forming in the axis of the amylose helices are seized, besides the energy of hydrogen bonds, by the resulting dipole moment, too.

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