been necessary lately to utilize both cottonseed hulls and corn cobs, and other raw materials must be taken into consideration in connection with further expansion of the industry.

Before World War II it seemed reasonable to consider that even the cheapest by-product of the annual crops could not compete successfully with petroleum as a source of raw material for the chemical industry. Now, in the face of depleted petroleum resources, it is conceivable that the price of petroleum may increase more rapidly than the cost of farm by-products. Consequently, the outlook for a chemical industry, based on annual crops, appears encouraging.

One of the serious drawbacks to their use in this field is the expense of transporting cheap, bulky materials to a central plant for chemical processing, and consequently one of the problems on which interested research workers will concentrate effort will be the development of processes and equipment by means of which intermediate and crude chemicals may be produced on the farm itself, in order to reduce the bulk of the material that must be transported to the plant where ultimate reaction or purification is to take place.

Under all the circumstances, even with the threat of a flood of by-product chemicals from the petroleum industry, the long future of the industrial production of chemicals from farm by-products may be considered sufficiently hopeful to justify continued and increasing expenditure for research in that field.

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FURFURAL FORMATION AND BEHAVIOR

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The kinetics of formation of furfural are discussed briefly. The stability of furfural is considered in some detail, attention being given to such factors as autoxidation, and decomposition by acids and heat. Various stabilizing agents are evaluated. Deaeration of the system is recommended in all processes employing furfural at elevated temperatures. From the standpoint of its chemical behavior, furfural is considered as an aldehyde and as a heterocyclic compound. The etheric, dienic, and aromatic properties of the nucleus are discussed with appropriate illustrations.

PENTOSAN-containing agricultural residues are known to be the raw materials from which furfural is produced. Little discussion of this general subject is needed, except to point out some of the factors which influence the selection of one particular source in preference to another.

From a theoretical standpoint furfural might be made from a great many agricultural materials, but in practice, economic considerations limit the choice to a comparatively small number. Cost is the most important factor; the yield of furfural averages only about 10% of the processed raw material. Low-priced furfural is therefore dependent upon low-cost raw material and such items as collection, handling, and shipping charges. In general, a suitable source of furfural should be available in large tonnages within a convenient shipping radius of the producing plant. Today the major raw materials are those listed in Table I, which also includes the potential furfural content of each. The latter represents the amount of furfural which can be obtained in the A.O.A.C. (*1*) analytical procedure for determination of pentoses and pentosans. Actually, it is only 88–90% of the theoretical amount if all the pentose is xylose, since the analytical method gives only this yield of furfural from pure xylose.

The potential furfural content, average natural moisture content, and bulk density are three additional factors which influence choice of a particular raw material. Jointly they determine the amount of furfural which can be produced per cycle in a digester of given volume. Consider, for example, the case of rice hulls; the potential furfural content is relatively low by comparison with that of oat hulls or of corn cobs. The higher bulk density of the rice hulls, however, permits a greater weight to be charged to the digester, so that, from the standpoint of pounds of furfural produced per charge, there is comparatively little penalty in using rice hulls as a source of furfural. This is not true of several other potential raw materials.

KINETICS OF FORMATION

In the process employed today for the production of furfural, the pentosan-containing raw material and dilute sulfuric acid are charged to a large, spherical, rotary digester which is then set in rotation. Steam is introduced to bring the charge to a selected conversion temperature, at which point a vapor outlet valve is opened to permit removal of furfural in the form of a steam distillate which passes directly to the recovery system. Steaming is continued until the furfural content of the vapors from the digester decreases below the practical level dictated by economic factors. By appropriate adjustment of operating temperature and acid concentration, the digestion cycle can be varied over wide limits of time.

This brief description of the commercial process shows that the conversion of pentosan to furfural is handled as a one-step procedure. However, it is recognized that there are several intermediate steps in the over-all reaction. The first of these

Table I. Major Sources of Furfural

Raw Material	Potential Furfural, % on Dry Basis
Corn cobs	23–24
Oat hulls	21–23
Cottonseed hull bran	20–23
Rice hulls	12–13

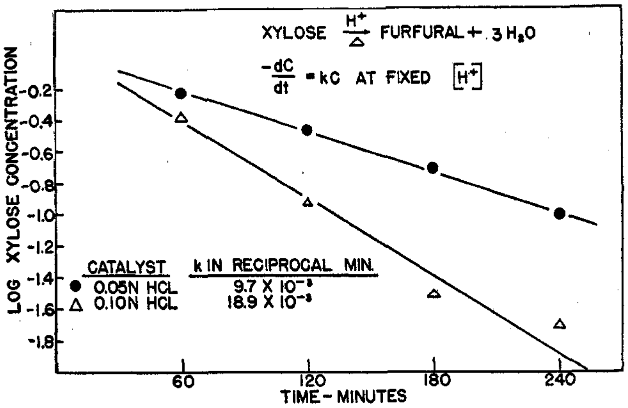

Figure 1. Rate of reaction of xylose at 160° C.

involves the acid-catalyzed hydrolysis of pentosan to pentose, which has been rather extensively studied by Bryner, Christensen, and Fulmer (*2*) and by Dunning and Lathrop (*6*). These investigators have demonstrated that the pentosan in oat hulls and in corn cobs can be hydrolyzed almost quantitatively to pentose without appreciably attacking the cellulosic fraction of the raw material. It is also apparent from their work that, at a given acid concentration and temperature, the hydrolysis reaction takes place at a greater rate than does the succeeding step, conversion of pentose to furfural. Accordingly, under selected conditions, pentosans can be hydrolyzed largely to pentose with practically no furfural formation. As expected, the reaction is accelerated by an increase in temperature and/or acid concentration.

In all probability the second step of the over-all process, conversion of pentose to furfural, proceeds by way of one or more intermediate products, although these have not been isolated to date. The system offers an interesting study in chemical kinetics complicated by several side reactions. Work in this laboratory (with xylose) has shown that the rate of disappearance of pentose in aqueous, acidic medium follows a first-order rate expression. This is illustrated in Figure 1, which also gives evidence that the reaction is first order with respect to hydrogen ion concentration. At the concentrations and temperature employed, doubling the acid strength would essentially double the hydrogen ion concentration. Accordingly, the rate constant is twice as great in 0.1 *N* hydrochloric acid as it is in 0.05 *N* hydrochloric acid.

In other words, the rate of disappearance of pentose is proportional to pentose concentration and to hydrogen ion concentration. Thus the reaction is at least second order, but it can be reduced to a first-order relation for any single set of conditions. Additional studies have shown that the rate approximately doubles for each 10° C. increase in temperature.

From the standpoint of furfural yield, side reactions contribute to loss of product. For example, the direct destruction of furfural by acid must be considered as proceeding simultaneously with formation of furfural. (Data on the extent to which this reaction occurs are given later in this paper in a discussion of the stability of furfural.) In addition, indirect evidence was obtained for a reaction between furfural and an intermediate to give resinous products. Other reactions may be involved which have not yet come to light; furfural or an intermediate product may react with lignin or some other component of the original pentosan-containing raw material.

Figure 2 presents a simplified diagrammatic summary of the over-all process. Pentosan is hydrolyzed to pentose, which is converted in two or more steps into furfural. Loss of furfural is due, in part at least, to side reactions *C* and *D;* reaction of furfural with an intermediate, *D*, contributes to decreased yield in a double-barreled manner.

If this picture is complete, removal of furfural from the reaction zone as rapidly as the furfural is formed should permit quantitative yields. Accordingly much effort has been expended in devising means for such instantaneous removal. Rapid steam distillation during conversion is the method now employed, but economics limit the amount of steam which can be expended per pound of furfural produced.

GENERAL PROPERTIES

Commercial furfural is a pale yellow liquid with a characteristic odor familiar to laboratory men and plant personnel working in this field. Its general properties are well known and need no comment at this time, except for a few remarks on the boiling characteristics and impurities.

Furfural has a very pronounced tendency to superheat, so that the boiling range varies considerably according to the rate of distillation and the method of supplying heat. For example, a typical Engler distillation may show a range in the neighborhood of 11° C. or more from first drop to dry point. On the other hand, careful fractionation through a Todd (*18*) column shows that fresh technical furfural is constant boiling to the extent of at least 98%. In this fractionation the presence of a small amount of water is responsible for a low boiling point for the initial few tenths of one per cent of distillate.

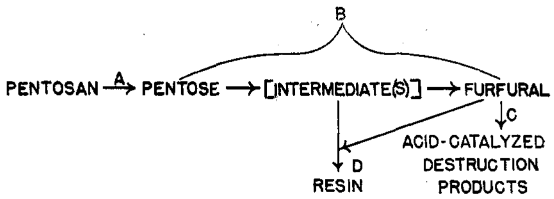

Figure 2. Summary of over-all process

The known impurities in technical furfural are water (approximately 0.1%) and a trace of acetic acid. In addition there is a nonvolatile or high boiling acidic material, probably a high-molecular-weight fatty acid derived from the raw material source of furfural. The total acidity of the fresh technical product is 0.02 equivalent per liter or less, of which 60–65 equivalent % is volatile and is mainly acetic acid. On this basis acetic acid is present in furfural to the extent of approximately 0.06% by weight, or less. The identity of the nonvolatile acidic impurity is unknown, but estimation from polymer determinations indicates that it may amount to a maximum of 0.3% in fresh technical furfural. Thus the impurities—water and acidic products—total only 0.4–0.5% of the marketed product, which is in good agreement with analytical data for the furfural content.

STABILITY OF FURFURAL

The stability of furfural is an interesting subject which merits considerable attention. We shall consider, in some detail, four factors which contribute to decomposition of furfural and attempt to give some expression of the magnitude of the changes which occur under various conditions.

Autoxidation. Many investigators have noted the slow increase in color of furfural and the simultaneous development of acidity which occur during long-term storage. It has now been demonstrated that these changes are due to autoxidation, that acidity and color are interrelated, and that oxygen is necessary for their development (*5*). Correlation of acid formation with oxygen consumption is shown in Figure 3. In this experiment technical furfural was shaken in an oxygen atmosphere at room temperature; this greatly accelerated the rate of autoxidation on two scores, (*a*) by providing contact with pure oxygen and (*b*) by continuously exposing a fresh surface of furfural by

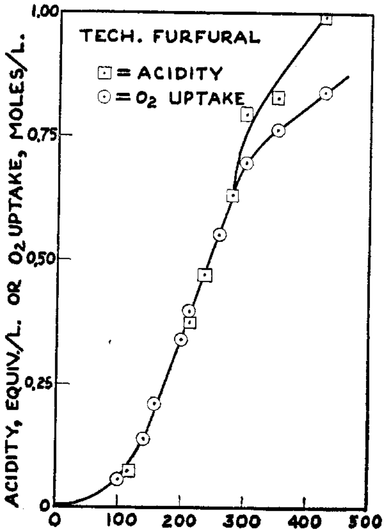

Figure 3. Relation between autoxidation and acid formation

agitation. Acid formation (in equivalents per liter of furfural) closely parallels oxygen uptake (in moles per liter) for a considerable period, after which they part company. In general, at the conclusion of highly accelerated experiments of this type approximately 1.2–1.4 equivalents of acid are formed per mole of oxygen absorbed. This ratio may vary, however, depending upon the rate of autoxidation, since, as will be shown later, one of the formed acids polymerizes to high-molecular-weight products of lower acid number.

Figure 4 illustrates the results obtained in another experiment in which various samples of furfural were similarly reacted with oxygen in the shaker apparatus. In this case acidity was not measured, the progress of autoxidation being gaged solely in terms of oxygen consumption. There are several significant facts to be noted:

First, autoinhibition of the autoxidation reaction is clearly indicated by the three curves in the upper portion of the figure. From this and other tests it is estimated that autoxidation practically ceases when some 7–8% of the furfural has been destroyed.

The pronounced effect of certain additives is also apparent from this experiment. Reference to the composite curve at the bottom of Figure 4 reveals a powerful inhibiting action by tripropylamine as representative of a tertiary amine, and by hydroquinone as an example of a phenolic type of antioxidant. Sodium carbonate, however, was effective only with technical furfural and did not prevent autoxidation of the pure product. (In these two instances the two samples of furfural were washed with aqueous sodium carbonate and then dried under vacuum.) This seeming anomaly may be related to one other noticeable difference between pure and technical furfural—namely, the extended induction period in the case of the latter. There is no corresponding inertia to autoxidation on the part of pure furfural, but one does observe a short induction period when pure furfural is treated with sodium carbonate. Earlier (*5*) it was postulated that soap formation was responsible for this inhibition during the early stages, and subsequently it has been found that tripropylamine oleate, a furfural-soluble soap, inhibits autoxidation. It is important to observe that it is unnecessary to render furfural basic, in order for tertiary amines to suppress the reaction.

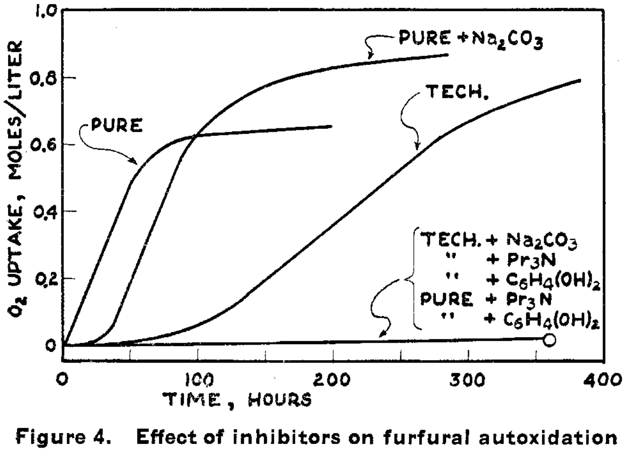

Figure 4. Effect of inhibitors on furfural autoxidation

These short-term, highly accelerated tests initiated a series of experiments designed to establish the relative efficiency of various inhibitors and to include a study of the effect of certain metals on the rate of autoxidation. In addition, it was desired to demonstrate conclusively that oxygen is necessary for the development of acidity in furfural under storage conditions.

A few of the results are presented in Table II. In these tests the furfural samples were stored in glass bottles, loosely plugged to permit free access to air where indicated. The pro-oxidant effect of iron is apparent by comparison of lines 1 and 2. Additional tests, not shown, indicate that tin and aluminum are much less pro-oxidant, and that copper may be antioxidant. However, the sample containing copper darkened in color even more rapidly than the control sample and, at the conclusion of the experiment, was found to have a high ash content. Accordingly any pronounced antioxidant activity on the part of copper is doubtful based solely on measurement of acid formation. It will be necessary to check oxygen uptake in order to establish the action of copper.

The inhibiting action of tripropylamine is evident by comparing lines 3 and 4 with lines 1 and 2 (Table II). The presence of iron does not appear to decrease its effectiveness materially. In similar long-term tests phenolic antioxidants, hydroquinone and catechol, were found to be quite ineffective in contrast to the fine showing they made in the shorter storage experiments (Figure 4). In general, it appears that inhibitors merely extend the induction period, during which time the rate of autoxidation (acid formation) is slow. When the induction period is over, the additive exerts no further effect and acid formation proceeds apace. Thus, in the type of test described by Table II, catechol showed strong inhibiting action for some weeks, but at the conclusion of the experiment there was little to choose between it and the control sample. Tertiary amines extend the induction period for a much longer time and thus may be recommended for use in some instances. However, these agents cause some color formation immediately on addition to furfural, and although this color does not increase in intensity during the extended period of effectiveness, it is a definite disadvantage to certain users.

To date, the only known means of storing furfural which ensures a light-colored product of low acidity is to provide an inert atmosphere. The last two lines in Table II demonstrate that storage under nitrogen completely prevents acid formation. A similar result was obtained with carbon dioxide, although in this case it was necessary to expel dissolved gas in order to ascertain the true acidity of the furfural.

The results presented thus far might conceivably give great concern to prospective users of furfural, unless it be understood

Table II. Six-Month Storage of Technical Furfural

(Conditions: room temperature; 1 liter furfural, approx. 113 sq. cm. surface exposure; iron added, 95 sq. cm. surface area; initial acidity, 0.013 equivalents per liter)

Atmosphere	Iron	Inhibitor	Final Acidity, Equiv./Liter
Air (free access)	No	None	0.397
Air (free access)	Yes	None	0.598
Air (free access)	No	0.1% TPA[a]	0.075
Air (free access)	Yes	0.1% TPA	0.079
N_2 (sealed)	No	None	0.015
N_2 (sealed)	Yes	None	0.015

[a] TPA = tripropylamine.

that the data are based on greatly accelerated tests. Actually, as might be anticipated, the rate of autoxidation is a function of the surface area exposed per unit volume of furfural (*5*). In short term tests in the shaker apparatus this ratio approached infinity—hence the rapidity of reaction. In the longer-term experiments just described, the ratio was still greatly in excess of that in normal storage. The authors measured the progress of acid formation in 55-gallon steel drum storage and found that, over a period of one year, the acidity increased from an initial value of 0.010 to only 0.012 equivalents per liter, the drum being kept full for the entire period. The earlier data are presented to demonstrate that autoxidation can become serious if given an opportunity.

Stability to Acids. Earlier in this paper mention was made of the destruction of furfural by acids. That certain furan compounds are sensitive to acidic reagents is well known, although almost without exception the information available is of a purely qualitative nature.

However, in connection with these studies on the kinetics of furfural formation, it was necessary to determine the extent to which this aldehyde is destroyed in aqueous, acidic medium. As will be shown, the reaction rate is not nearly so rapid as might have been supposed by some investigators in this field.

In carrying out this investigation, furfural was heated with aqueous solutions of various acids in various concentrations. The data obtained are reported in detail elsewhere (*19*). Briefly, they establish that the rate of destruction is proportional to the concentration of furfural and to the hydrogen ion concentration, and that, for a given set of conditions, the rate follows the equation for a first-order reaction. It should be observed that formic acid is a product of the reaction, probably as a result of hydrolytic fission of the aldehyde group. Thus, water is probably a reactant, but, in the experiments under consideration, it was present in overwhelming abundance; hence, its concentration did not change significantly. In addition, the formic acid which is formed does not materially affect the rate of destruction until its contribution to the initial hydrogen ion concentration becomes significant. Thus in dilute aqueous, acidic medium the reaction is pseudounimolecular and may be described by a first-order rate expression for an extended period.

Using 0.1 N sulfuric acid at various temperatures in the range 160–210° C., the rate constants were derived and applied to the Arrhenius equation, which was calculated to be:

$$\log k = \frac{-E}{2.303\,R}\,\frac{1}{T} + C = -\frac{4365}{T} + 7.145$$

Values for k so calculated are in terms of reciprocal minutes, and they apply only to the destruction of furfural in 0.1 N sulfuric acid. For a different acid system the k value may be corrected in accordance with the fact that k is directly proportional to the hydrogen ion concentration.

The discussion thus far may have little direct relation to the acid destruction of furfural in nonaqueous medium. It is quite possible that the reaction mechanism in the latter case is completely unrelated to that which prevails in water solution.

A black jellylike resin results when furfural is brought into contact with concentrated sulfuric acid; this jelly contains much unchanged furfural which is easily recoverable by distillation, leaving a finely divided, infusible, and insoluble solid. Many other acidic reagents have a similar effect on furfural, but quantitative information is lacking.

The following experiment serves to give some idea of the extent of resinification in one specific instance. Technical furfural containing 4% by weight of concentrated sulfuric acid was allowed to stand in the room for 9 days. At the end of this time the resinified material was leached exhaustively with water to remove the acid and unreacted furfural. The dry resin obtained amounted to only 7% of the original furfural.

It would appear, therefore, on the basis of the information at hand, that rather drastic conditions are required to produce extensive destruction of furfural by acids either aqueous or nonaqueous. This is not too surprising when it is recalled that furfural is formed in an acidic medium.

Thermal Stability. Some years ago data were published on the thermal stability of furfural (*4*). The product studied at that time was a refined grade, since the object of the work was to obtain information which might be applicable to solvent refining processes. In these processes furfural is generally recovered in a highly refined state after having been circulated once through the operating system.

Only a brief summary of the results will be given here. The technique involved heating furfural in sealed glass tubes from which almost all of the air in the void space had been removed. Accordingly autoxidation was essentially avoided, and furfural was found to be quite resistant to thermal breakdown. Many hours of exposure were required, even at temperatures as high as 230° C., to produce detectable changes in the physical properties, with the exception of color. The extent of decomposition was found to be within the limits of analytical error for an extended period. Exposure at 180° C. for as long as 185 hours showed that only a few tenths of one per cent of the furfural had been destroyed. Increase in temperature accelerated the reaction, so that, at 230° C., 3–5% of the furfural had been destroyed in 75 hours. Contact with metals did not increase the rate of destruction at these temperatures.

The mechanism of thermal breakdown of furfural has not been elucidated. It is known, however, that water is split out and that the polymer formed is nonacidic in character.

Summary. The four modes of destruction of furfural which have been discussed are illustrated diagrammatically in Figure 5. All of these reactions are accelerated by an increase in temperature. In the earlier remarks each was considered separately, although it is conceivable that all four could proceed simultaneously under certain conditions.

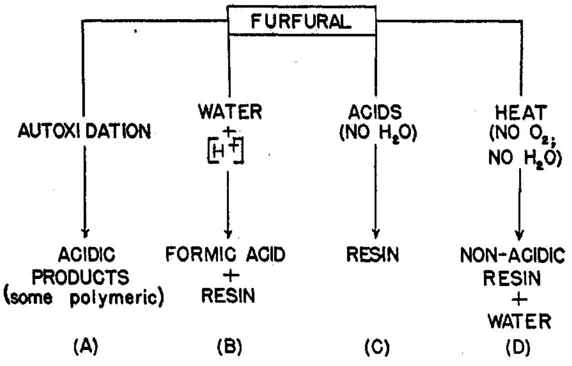

Figure 5. Four modes of furfural destruction

Consider, for example, a hypothetical case in which furfural is heated in air. Reactions A and D can both take place. A gives acidic products and thus promotes C, while the water formed as a result of reaction D in conjunction with the acid from A permits reaction B to occur. The saving grace is that reaction D is slow, and that B and C require rather strongly acidic conditions in order to become significant. Returning to our proposed system, however, if air had been excluded, destruction would have been essentially limited to thermal decomposition, the slow reaction D.

Thus reaction A, autoxidation, is something to be avoided if at all possible. In this connection it should be pointed out that an increase in temperature greatly accelerates the rate of autoxida-

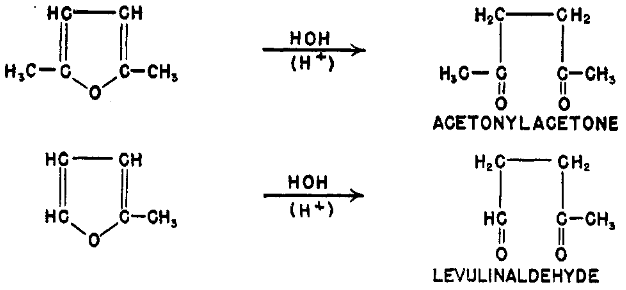

Figure 6. Hydrolytic fission of furan ring

tion and, for all practical purposes, nullifies the beneficial effect of the inhibitors which were discussed earlier. Accordingly, in those processes employing furfural at elevated temperatures, it is recommended that the system be deaerated and kept free from oxygen. Such a precaution is calculated to decrease furfural losses and to eliminate corrosion difficulties which might otherwise arise because of the acidic products of autoxidation.

CHEMICAL BEHAVIOR

The chemical behavior of furan compounds is determined jointly by the nucleus and by the groups attached thereto. The following discussion summarizes briefly the various chemical characteristics of furfural, with occasional reference to other furan compounds where this seems desirable.

Aldehyde Reactions. The aldehyde reactions of furfural are almost exactly like those of benzaldehyde. It is readily oxidized to furoic acid, undergoes the Cannizzaro reaction with aqueous alkalies, and gives furfuryl furoate with sodium furfuroxide. Under the influence of potassium cyanide, furoin is obtained, in a method analogous to production of benzoin in the benzene series. Condensation with ammonia gives hydrofuramide, the furan analog of hydrobenzamide.

Furfural also participates in the Perkin and Claisen condensations, and other related syntheses involving reaction of the aldehyde with a compound possessing active hydrogen atoms. Thus, condensation with acetone yields furfuralacetone, and furylacrolein is obtained with acetaldehyde. With primary amines the corresponding furfural imines or Schiff's bases are obtained.

It is evident, therefore, that furfural enters into the normal reactions characteristic of the aldehyde function.

The nuclear reactions are also interesting because of the polyfunctional nature of the furan ring. Furans can react as ethers, as dienes, and in the manner commonly designated as aromatic. The extent to which these various properties contribute in a given reaction is influenced by the nature of substituent groups and by the demand of the attacking reagent in the environment provided. This possibility for a variety of reactions to occur probably accounts for the low product yields obtained in many reported instances.

Etheric Nature of Ring. If ease of hydrolytic fission of the nucleus be taken as a measure of etheric character, it is indicated that the properties of furfural are less pronounced, in this respect, than in such furan compounds as 2-methylfuran and 2,5-dimethylfuran. As in the case of other ethers, the hydrolysis reaction is catalyzed by acidic reagents, the furans being converted into 1,4-dicarbonyl compounds (Figure 6).

For example, the ring in 2,5-dimethylfuran is readily opened under the influence of dilute acids. Almost quantitative yields of acetonylacetone may be obtained under the proper conditions (*20*). 2-Methylfuran is ruptured in a similar manner to give a resinous product. Using alcohol and a trace of hydrochloric acid instead of aqueous acid, Harries (*12*) reports the acetal of levulinaldehyde as the product in this instance.

Furfural, however, is less prone to ring rupture than are these two alkylated furans. Relatively long exposure at elevated temperatures is required to bring about extensive destruction by dilute aqueous acids (*19*). The products of destruction are formic acid and a black resin, which Marcusson (*14*) postulated to be a condensation polymer of succindialdehyde, although this has not been definitely established.

In the cases cited, the rate of ring opening is accelerated by increasing the concentration of acid catalyst. More specifically, with regard to furfural, our studies have shown that the rate is directly proportional to the hydrogen ion concentration. Thus, the hydrolysis reaction involves an attack on the furan nucleus which is promoted by hydrogen ion, and the reduced rate, in the case of furfural, must be due to an inhibiting effect of the aldehyde group. This effect of hydrogen ion would appear to be related to a donor tendency on the part of the nucleus—conceivably coordination of the nuclear oxygen atom with a proton to form an oxonium ion, with resultant weakening of a C—O bond and/or relative decrease in electron density at the alpha carbon atoms. As suggested by Remick (*16*), the capacity of the nuclear oxygen atom to act as a donor would be diminished by negative ring substituents such as CHO, COOH, and NO_2.

Dienic Nature of Ring. The dienic properties of the furan nucleus are sufficiently well developed in furan, alkylfurans, halogenofurans, and certain others to permit ready participation in the Diels-Alder reaction with maleic anhydride (*15*). The anhydride adds 1,4 to the ring to form the normal cyclic adducts, as illustrated in Figure 7 for the case of methylfuran.

This type of reaction has been explained as being due to contribution of an electron pair by the dienic reactant to the electron-poor double bond of the anhydride. In other words, the particular furan compounds cited possess nucleophilic properties, a tendency to donate electrons to an acceptor center such as is provided by maleic anhydride. It is true that these furans will not add, in the normal manner, weaker dienophiles such as acrolein, methyl vinyl ketone, etc.; from this it may be concluded that the donor tendency of the diene system in furans is less pronounced than in a compound like butadiene.

In the case of furfural, however, no addition product is obtained even with the strongly dienophilic maleic anhydride, under conditions which permit almost quantitative reaction in the case of alkylfurans. Either no reaction occurs, or else the adduct is so loosely bound that it defies isolation. Thus, the nucleus in furfural is, apparently, less nucleophilic than that in furan or methylfuran, no doubt as a result of the electronegative formyl group, which would tend to decrease the electron density in the nucleus. Such a tendency, if sufficiently pronounced, would lead one to suspect that furfural, and other negatively

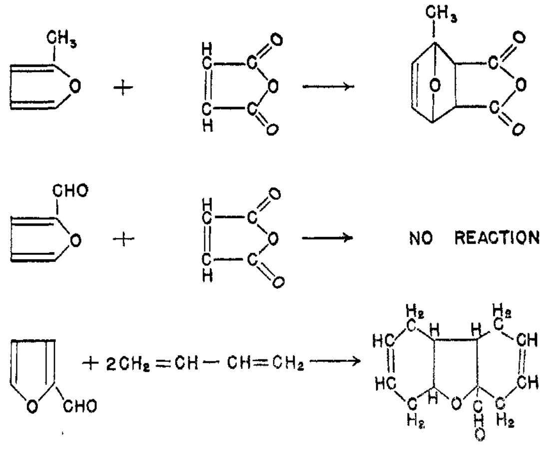

Figure 7. Behavior of furans in Diels-Alder reaction

substituted furans, might exhibit dienophilic or acceptor activity in a Diels-Alder reaction with a suitable diene. Recent experimental work indicates that this does occur in the system furfural-butadiene (*13*). These compounds react at elevated temperatures in such a manner that two molecules of butadiene add to one molecule of furfural to form an unsaturated aldehyde which has been assigned the structure shown in Figure 7.

Thus, on treatment with maleic anhydride, furfural fails to act as a diene and can actually furnish an acceptor center to an active diene like butadiene.

That the nucleus in furfural does possess some dienic character, however, is indicated by a consideration of the products obtained on autoxidation (Figure 8).

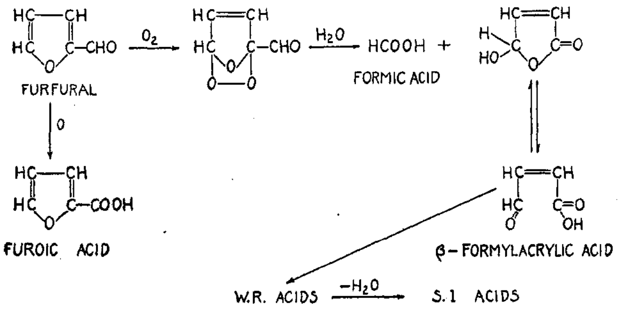

Figure 8. Proposed scheme for autoxidation of furfural

In contrast to benzaldehyde, which under similar conditions gives benzoic acid as virtually the sole end product, furfural gives only minor quantities of furoic acid on autoxidation. The chief acids formed are formic, β-formylacrylic, and polymeric acids related to the latter. It is felt that the most reasonable explanation of the over-all reaction is a preliminary 1,4- type addition of oxygen to the furan ring to form an intermediate peroxide, which, because of the nuclear oxygen atom, has the structure of an ozonide. In the presence of water this intermediate, which could not be isolated, decomposes as shown in Figure 8.

It might be argued that perfuroic acid is the intermediate formed initially and that this is the agent, rather than oxygen, which attacks the ring in furfural to give the products found. If this were true, however, one mole of furoic acid should be formed for each mole of oxygen consumed. Actually, furoic acid is found in only one tenth the quantity anticipated on this basis. Furthermore, if furoic acid be considered the precursor of the formylacrylic acid, one would expect carbon dioxide as a decomposition product rather than formic acid which was found.

Although only a small quantity of the unstable formylacrylic acid could be isolated, its presence is of theoretical importance in that it is the precursor of the resinous products of autoxidation, the products here termed the "WR" (water-soluble resin) acids and the "SI" (solid indicator) acids. The former possess a carbon and hydrogen content corresponding to a polymer of formylacrylic acid, and the SI acids appear to be formed by loss of water from the WR acids. These are the products which are primarily responsible for the dark color which develops in furfural on storage.

Thus, the major point of attack during autoxidation of furfural is the nucleus rather than the aldehyde group, and it is quite probable, although not definitely established, that the course of reaction involves a dienic-type addition of oxygen to the ring. Schenk (*17*) also proposes this mechanism to account for the results obtained in his studies relating to the autoxidation of furan and 2,5-dimethylfuran.

It is interesting to observe that, by contrast, liquid-phase oxidation of furfural in an alkaline medium gives furoic acid exclusively. Thus alkaline agents would appear to inhibit the dienic properties of the furan nucleus.

AROMATIC NATURE OF RING. In taking up the next subject of this paper, aromatic behavior of furfural, it is considered sufficient merely to report those reactions leading to nuclear substitution. The controversial issue concerning the relative aromaticity of furans as compared to other types will not be discussed, nor will the various substitution mechanisms which have been proposed.

Furfural was first nitrated, as the diacetate, by Gilman and Wright (*7*). The reaction was carried out in acetic anhydride, and the entering nitro group oriented to the 5- position. Later these investigators by-passed the intermediate step of preparing furfural diacetate and nitrated furfural directly in acetic anhydride (*8*). This reaction forms the basis for the commercial production of the new chemotherapeutic agent, 5-nitro-2-furfural semicarbazone, marketed by Eaton Laboratories as Furacin.

The halogenation of furfural likewise results in substitution at the 5- position. Treatment of furfural diacetate with bromine gives 5-bromo-2-furfural in 25% yield (*9*). The preparation of the corresponding chloroaldehyde was found to give yet lower yields (*10*) until recently, when Chute and Wright (*3*) reported on their observation of the catalytic effect of sulfur and of benzoyl peroxide. They chlorinated furfural directly in carbon disulfide to which had been added small amounts of these two agents. 5-Chloro-2-furfural was obtained in 33% yield, compared to 1–2% when the reaction is conducted in sulfur-free solvent with no added peroxide.

Alkylation of furfural by the Friedel-Crafts procedure has given interesting results. The work of Professor Gilman and his students (*11*) has established, for instance, that alkylation with isopropyl chloride gives 4-isopropyl-2-furfural instead of the 5-isopropyl derivative which would have been expected in view of the preferred alpha substitution of furan compounds. In the case of butyl and amyl chlorides, the normal orientation was observed, the entering alkyl group substituting at the 5- position.

This brief discussion illustrates that nuclear substitution reactions can be carried out with furfural. All are accompanied to a greater or lesser extent by decomposition reactions involving furfural itself, an intermediate formed during the course of the reaction, or both.

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