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RADIATION-INDUCED REACTIONS OF SOME FURAN CHEMICALS

J. J. J. Myron
W. W. Parkinson

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REACTOR CHEMISTRY DIVISION

RADIATION-INDUCED REACTIONS OF SOME FURAN CHEMICALS

J. J. J. Myron and W. W. Parkinson

AUGUST 1969

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RADIATION-INDUCED REACTIONS OF SOME FURAN CHEMICALS

J. J. J. Myron* and W. W. Parkinson

ABSTRACT

The products of irradiating tetrahydrofuran, furfural, tetrahydrofurfuryl alcohol, and dimethyl sulfoxide, individually and in mixtures, have been investigated for commercial potential. Solutions of pentadiene in furfuryl alcohol, in tetrahydrofurfuryl alcohol, and in furfural have been irradiated and examined more briefly. In tetrahydrofuran and dimethyl sulfoxide only were products observed in the desirable molecular weight range of dimers and trimers. In these cases the yields were not over 5 molecules per 100 ev, inadequate for commercial exploitation.

The major radiation product from furfural was a complex polymer at the rate of 4 molecules of furfural incorporated per 100 ev. A considerably higher polymer yield, probably about 13 molecules incorporated per 100 ev was observed in solutions of pentadiene in furfuryl alcohol.

INTRODUCTION

Radioactive isotopes are becoming more and more available as by-products of the ever-increasing number of nuclear reactors. This growing supply of radiation sources has inspired a search for radiation-induced chemical reactions of commercial potential. On the other hand, processing by radioisotopes is relatively expensive in terms of radiation energy deposited per unit weight of irradiated material because of handling, shielding, and plant equipment costs.

The usual radiation-induced processes have yields of one to eight molecules reacted or produced per 100 electron-volts of energy absorbed (G = 1-8).** To be economically feasible with these yields, a process must either give products commanding a high price or involve polymers of high molecular weight in which a small amount of cross linking or scission (on a weight basis) results in appreciable changes in mechanical properties.

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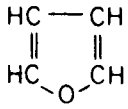
**In the terminology of radiation chemistry, the radiation yield is expressed as the "G-value": the number of molecules produced or reacted per 100 ev of energy absorbed.

It is possible, however, to initiate chain reactions with the free radicals and ionic species generated by radiation just as chain reactions are initiated by chemically produced free radicals. Such reactions may have very high yields, G = 10^3-10^5 molecules per 100 ev. Furthermore, initiation by radiation offers the following advantages: (a) there is no catalyst contamination of the final product, (b) usually the reaction can be carried out at lower temperatures than with chemical initiation, and (c) better control of the rate and extent of the reaction is possible by variation of dose rate and total dose.

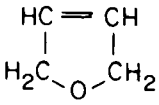
Various chain reactions have been reported in the literature involving the addition of polar compounds to olefinic groups.[1,2] Furan and furan-type compounds, which are cyclic ethers, have a slightly polar character (due to the ether function) and also have two double bonds in their structure. They, therefore, were thought to be attractive candidates for investigation.

Furan itself (A) has proven to be moderately radiation-resistant, probably due to some resonance stabilization of the ring. Therefore, related molecular structures such as dihydro-(B) and tetrahydro-(C) furans, as well as derivatives with a side chain attached to the furan ring, were also considered as possible synthesis agents.

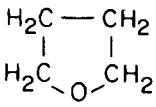
(A) Furan



(B) Dihydrofuran

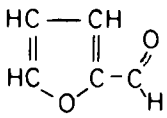


(C) Tetrahydrofuran



Availability at low cost is another feature of the furan chemicals since furfural (2-furaldehyde) (D) is produced by simple dehydration of

(D) Furfural

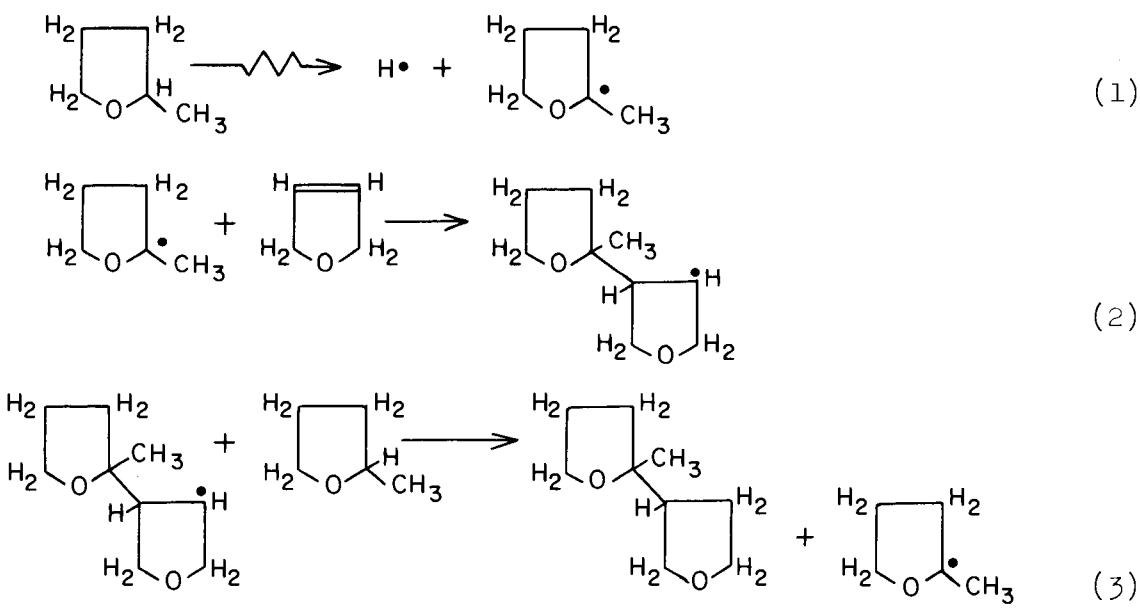


the pentosans of grain hulls, corn cobs, and other agricultural by-products. Furthermore, one-step modifications such as hydrogenation of the ring or partial or complete reduction of the aldehyde group yield a

variety of derivatives of low cost having a side group at the 2 position of the furan ring.[3,4] The dimeric and trimeric coupling products from these compounds could be expected to find uses as non-volatile solvents, plasticizers, chelating agents, humectants, and synthesis intermediates.

Products of molecular weight greater than trimers are difficult to separate and consequently are troublesome both to study and to process industrially. In this investigation, when polymeric products appeared, their yields were sometimes estimated, but they were not studied extensively. Since the more active furan derivatives can be made to polymerize under relatively moderate chemical conditions, polymeric products were not considered good candidates for utilizing radiation.

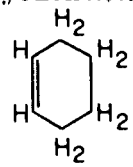
The singly substituted furans and tetrahydrofurans would appear to be favorable chemicals as they possess a tertiary hydrogen atom that would be expected to be more labile than primary or secondary hydrogen atoms. This lability would improve chances of the formation of radicals that could propagate high-yield chain reactions of dimeric or trimeric products. A typical scheme for the generation of such bicyclic ethereal molecules involving 2-methyl-tetrahydrofuran and dihydrofuran is as follows



The radical chain carrier in this sequence is the 2-methyl-tetrahydrofuran radical.

The initial studies on cyclic ethers with unreactive or no side groups demonstrated that product patterns were simple with one or two addition products dominating.[5] The yields were dependent on concentration, total dose, and on temperature but were below the chain reaction range at room temperature. The effects of these reaction conditions on the yields and the identities of the major products were studied for a simple system based on tetrahydrofuran as the furan chemical. Cyclohexene (E) was chosen as the unsaturate because its behavior under radiolysis

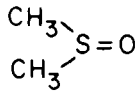
(E) Cyclohexene



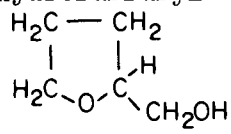
is well documented in the literature.[6,7] This system is discussed in detail in a companion report, but in brief, the major products were a high-boiling telomer and the codimer for which G = 1 at 20°C and 8 at 300°C.[8]

The yield at 300°C was too low for a chain reaction and this temperature was above the critical temperature for the system, the upper limit for convenient laboratory irradiations. It was apparent that solutions of greater reactivity should be investigated. Consequently, solutions containing tetrahydrofuran and dimethyl sulfoxide (F), furfural, tetrahydrofurfuryl alcohol (G), furfuryl alcohol (H), and 1,3-pentadiene (piperylene) (I) were studied and are discussed in this report.

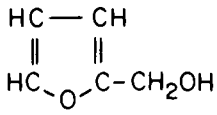
(F) Dimethyl Sulfoxide



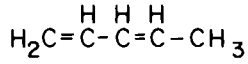
(G) Tetrahydrofurfuryl Alcohol



(H) Furfuryl Alcohol



(I) 1,3-Pentadiene



EXPERIMENTAL

Materials

Since the major aim of the program was to evaluate systems that would be of commercial use, no rigorous purification of materials was attempted. Instead, the highest purity chemicals that were available commercially were used throughout the investigation (see Table 1). Purification of furfural by vacuum distillation was carried out for certain selected irradiations, but the effects of minor impurities on yields and reaction mechanisms were not investigated for most materials.

Sample Preparation

As oxygen has been proven to be an efficient radical and electron scavenger, samples were irradiated under vacuum except where otherwise noted. The necessary degassing and ampoule sealing manipulations were performed with the aid of a conventional vacuum system that utilized Pyrex glass, "Veeco" metal valves, and glass-to-metal seals.

Initially, samples were prepared by vacuum distillation from reservoirs of the reagents in the vacuum system. Replacement of the neoprene sealing discs of the metal valves with polytetrafluoroethylene was necessary to eliminate attack by the furan chemicals. Because of the long distillation times required in the vacuum system, samples of high-boiling compounds were not distilled but were transferred in air to the ampoules which were subsequently evacuated and degassed.

All samples were contained in cylindrical Pyrex ampoules that connected to the vacuum system by ground glass joints. The samples were thoroughly degassed by repeated freeze-pump-thaw cycles. The coolant was liquid nitrogen (temperature = -196°C). Heavy-walled ampoules were necessary when furfural or tetrahydrofurfuryl alcohol was involved as these liquids showed a strong tendency to shatter the ampoules during freezing and thawing. After thorough degassing the ampoules were sealed off prior to irradiation.

Exploratory samples were generally of 2-ml volume but a number of runs were processed that were of 10- to 12-ml volume. The larger volume was necessary to facilitate ancillary analyses of the radiolytic products.

Table 1. Reagents for Radiolysis of Furan Chemicals

Compound	Boiling Point °C	Index of Refraction N_D^{20}	Manufacturer	Estimated Purity
Tetrahydrofuran	65.5-66.5	-	Matheson, Coleman & Bell	>95%
Furfural (2-furaldehyde) (Packed under inert atmosphere)	39-40 (at 5 mm)	-	Matheson, Coleman & Bell	>95%
Furfuryl Alcohol	80-81 (at 20 mm)	-	Matheson, Coleman & Bell	>95%
Tetrahydrofurfuryl Alcohol	-	1.4525	Aldrich Chemical Company	~97%
Dimethyl Sulfoxide (Density, 1.097; Water, 0.05%; Residue on Evap. 0.001%)	-	-	J. T. Baker Chemical Company	~95%
1,3-Pentadiene (Piperylene) (Mixture of cis and trans)	-	1.4338	Aldrich Chemical Company	~97%

Irradiation

Irradiations were performed with a ^{60}Co gamma-ray source. The majority of samples were irradiated inside a cylindrical assembly of encapsulated radioactive cobalt that was capable of imparting a dose of $\approx 1.0 \times 10^5$ rads/min in the samples. Temperature was maintained at 25 ±2°C by a water bath. A number of samples was prepared for irradiation in their solid state. For this purpose the samples were immersed in liquid nitrogen in a conventional Dewar flask and placed outside the ^{60}Co array. The dose rate in this position was $\approx 3 \times 10^3$ rads/min.

The radiation intensity was measured by the ceric sulfate dosimeter.[9] This in turn was calibrated against the "Fricke" (ferrous sulfate) dosimeter taking the yield of ferric ion as $G(Fe^{+++}) = 15.6$ (Ref. 10).

During low-temperature irradiations the liquid nitrogen in the Dewar was changed at least once every 16 hours in order to reduce the danger of explosion from the accumulation of ozone and liquid oxygen in the coolant. Ozone, when present in appreciable concentration, decomposes violently under gamma irradiation.

Product Analysis

The primary analytical tool utilized to determine the efficiency of a particular radiation synthesis experiment was gas chromatography. In such a system, if one can achieve reasonably short retention times for the original reagents, it can be expected that dimeric and even trimeric products can be detected and measured. The chromatograph employed was an F & M Model 500 with a Model 1609 flame ionization detector. This detector allowed the use of small injection volumes, 1 to 5 microliters (λ), but unfortunately resulted in a destructive analysis which precluded collection of chromatographic peaks for supplemental analysis. The columns used for these analyses were varied, depending upon the properties of the expected product.

Several irradiated samples were chromatographed on at least two different columns to eliminate the possibility that co-incident retention times would obliterate a radiolytic product. A variety of column temperatures ranging from 65-200°C was used to insure optimum conditions for analysis.

Ancillary analytical methods including infrared spectrometry, nuclear magnetic resonance spectrometry, thermogravimetric analysis, and elemental analysis were also used when necessary.

RESULTS AND DISCUSSION

Tetrahydrofuran - Dimethyl Sulfoxide

An examination of the products from irradiated tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and binary mixtures of the two was undertaken. The latter compound was chosen as a component as it is readily available as a by-product of the pulp and paper industry, it has moderate price, and is miscible in all proportions with THF. It also has widespread solvent properties and has been used as a solvent in radiation-induced polymerization systems.[11] It has been employed as a radiation protector in biologically significant systems.[12,13] However, the effect of radiation upon the sulfoxide itself and its role as a component in binary radiolysis systems appears to have received little attention.

Degassed liquid samples of (1:1) and (5:1) mole ratios of THF:DMSO solutions as well as the pure components were irradiated at room temperature to a dose of 1.2×10^7 rads. These samples and unirradiated samples of THF and DMSO were analyzed by gas chromatography on a 4' x 1/4" column containing silicone rubber (≈8% by weight) on Polypak 1 support. The column temperature was maintained at 205°C.

The chromatograms for all irradiated samples showed between 5 and 10 peaks of molecular weight less than that of the original reagents. These products represent decomposition rather than "synthesis," i.e., addition products. In the case of pure sulfoxide and pure ether, one of the peaks was a major one and the rest minor. Mixtures of THF:DMSO showed two major peaks with retention times identical to those obtained from the "pure" samples (Fig. 1).

Chromatography peaks of greater retention time, and hence presumably higher boiling point and higher molecular weight than the original reagents were observed in all irradiated samples. In the 100% DMSO and THF samples 3-5 such peaks were observed. However, as in the case of the decomposition products one peak in each case predominated. Calculations based upon assumed calibration factors showed that the major products

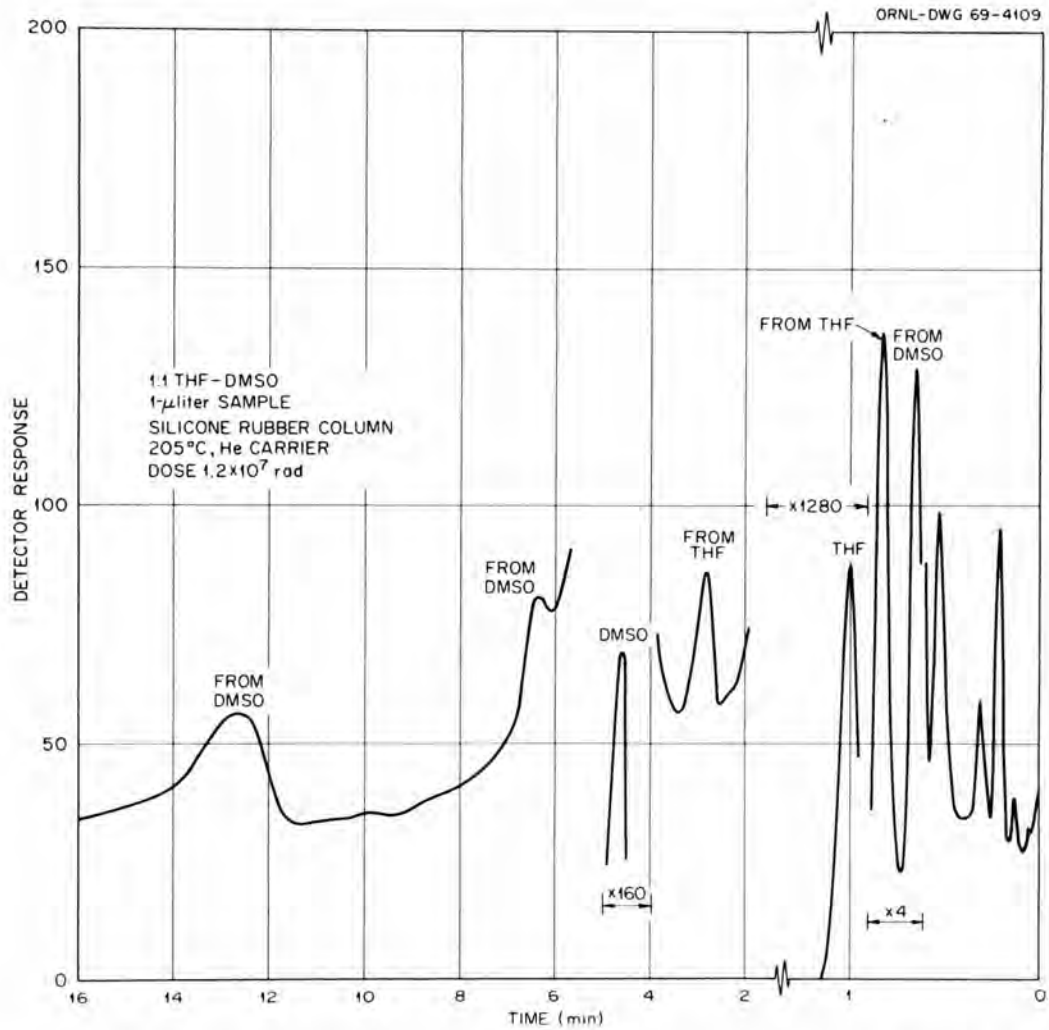


Fig. 1. Chromatogram of Irradiated Solution of Dimethyl Sulfoxide in Tetrahydrofuran.

(both decomposition and synthesis compounds) had yields of 4-10 molecules per 100 ev.* This magnitude of yield shows that no chain reactions were operative.

Results from the mixtures of the two components indicated that no "cross" reaction products (i.e., codimers, trimers, etc.), that could be detected by gas chromatography were present. In fact, the dominant, high molecular weight peak from irradiation of pure THF did not appear in the chromatogram of the THF-DMSO mixture and the major product in pure DMSO had decreased in the irradiated mixture. Apparently, DMSO inhibits the radiolysis of THF in some manner which does NOT involve the scavenging of THF radicals. The yields of decomposition products were not followed precisely enough to determine whether energy transfer or hydrogen atom transfer processes in the mixture increased these products while reducing the formation of the THF addition product.

Unirradiated DMSO is almost odorless. However, all irradiated samples that contained any DMSO had a distinct odor very similar to that of mercaptans. As methyl metcaptan is a major decomposition product of the sulfoxide upon prolonged refluxing,[14] the large product peak from DMSO of short retention time is probably methyl mercaptan.

Systems Involving Furfural

Formation of Addition Products and "Polymer"

Since the behavior of furfural itself under irradiation was not known, a 2-ml sample was degassed in the usual manner and irradiated to a moderate dose (45 Mrads). This was analyzed chromatographically by injection on the silicone column at a temperature of 205°C. Only one small peak with a retention time less than the furfural peak was detected. The only peak observed after the furfural itself was an impurity peak that was also present in the unirradiated furfural. It was concluded that there were no irradiation peaks in the range of dimers or trimers. However, it was observed that the usual deep brown color of

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*The calculation was based on the assumption that one molecular nucleus of DMSO or THF gives the same peak area both in the unreacted state and in the product molecules (dimers, trimers, etc.). While this assumption may not be precisely correct, it does furnish a basis for calculation of the G-value for molecules of initial reactant incorporated into products.

furfural was bleached by radiation to a pale yellow. Since the removal of color from chemical reagents can have commercial value, the bleaching was investigated further and is reported below.

In an effort to obtain a measurable quantity of radiation product, a second sample, prepared in the usual way was irradiated to a high dose, 740 Mrads, which converted it to a dark, reddish, transparent gel. This gel, or at least a large part of it, was insoluble in the common organic solvents (acetone, carbon tetrachloride, carbon disulfide, cyclohexene, etc.).

A portion of the gel was evacuated to remove unchanged furfural, and a hard brittle polymer remained from the gel. This material was thoroughly ground, mixed with spectroscopic grade KBr and pressed into a pellet for infrared analysis. This spectrum (Fig. 2a) differed from that of unirradiated furfural in having a strong, very broad asymmetric band at 3450 cm^{-1} that could be attributed to hydroxyl groups in the polymer. A control sample of furfural in a pressed disc proved this absorption was not due to sample manipulation. There were other radiation-generated infrared bands in the polymer and these are discussed below in connection with distilled furfural.

Evaporation of the gel to constant weight gave a residue that corresponded to a 28% conversion of the furfural to polymer. Two identical distillations of unirradiated furfural indicated a residue that averaged 1.0% of the total so that virtually all of the residue from the irradiated sample was a product of the radiolysis reaction and not distillation conditions. The 28% conversion corresponds to a G value of 4 molecules of furfural converted to polymer per 100 ev.

Under normal storage conditions, furfural develops dark-colored trace impurities and the color of the furfural stock used for the previous irradiations indicated that these impurities were present. To determine whether these impurities influenced the polymer yields and gelation dose, they were eliminated by vacuum distillation of a sample which was then outgassed, encapsulated and irradiated under the same conditions as previous specimens. A dose of 720 Mrads also transformed this sample into an amber gel. The percent conversion after vacuum evaporation to constant weight amounted to 29% (almost identical to that from unpurified

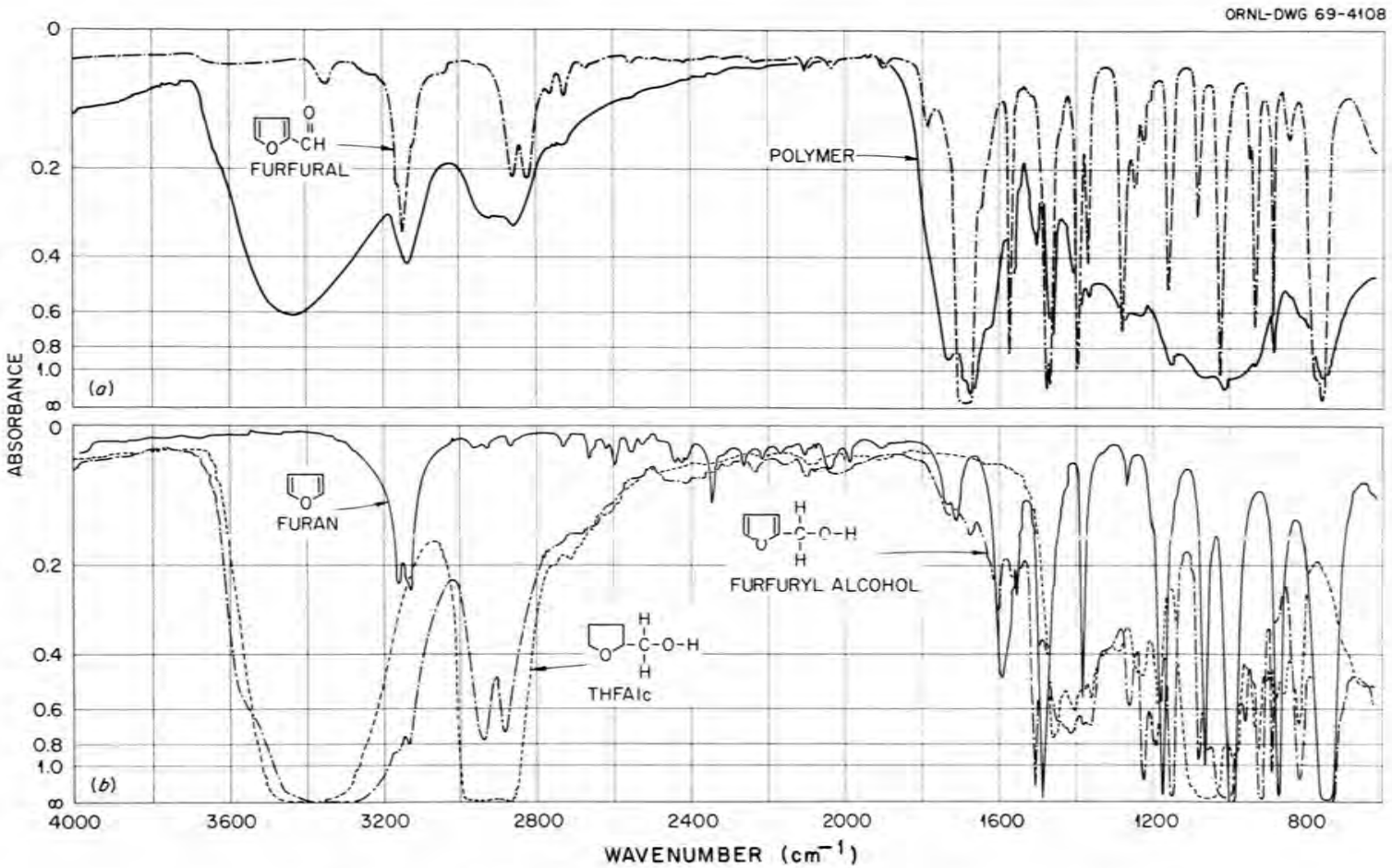


Fig. 2. (a) Infrared Spectrum of Furfural and Gel from Irradiated Furfural. (b) Infrared Spectrum of Furan, Furfuryl Alcohol and Tetrahydrofurfuryl Alcohol.

furfural). This again corresponded to a G value of 4 for aldehyde conversion to polymer.

The I.R. spectrum of the solid polymer from purified furfural was essentially the same as that of the gel from the unpurified specimen. Comparison of the spectrum of the solid polymer with the spectra of furfural, furfuryl alcohol, and other furan derivatives (Figs. 2a and 2b) provides several indications of the course of the radiation-induced polymerization. This comparison should indicate how similar this reaction is to the chemical polymerization. Specifically, we would like to know whether polymerization proceeds through addition at the carbonyl group in a benzoin-type condensation, or by addition of an H atom of the ring to this group, or whether addition to the furan ring itself is involved.

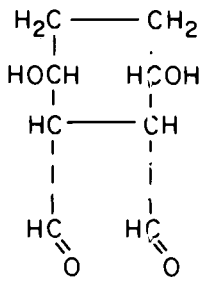
The spectral bands in furfural that are decreased in the polymer (Fig. 2a) include, first the C-H stretching band of the aldehyde group at 2820 cm^{-1}, which almost disappears. The band at 1680 cm^{-1} attributed to C=O stretching[15] is probably reduced although this strong peak is so near infinite absorption that zero errors and light scattering in the sample pellet make decreases in this band uncertain. Bands which are reduced with respect to a reference band at 2855 cm^{-1} are those at 1570 and 1460, attributed to asymmetric and symmetric ring stretching modes for 2-substituted furan rings.[16]

New bands in the polymer include the very broad and intense OH stretching mode at 3450 cm^{-1} already mentioned, a C—H stretching band at 2930, probably from the alcohol group, CHOH (as seen in furfuryl alcohol and in tetrahydrofurfuryl alcohol, Fig. 2b), a shoulder at 1620, possibly the stretching of a C=C group, a sharp band at 1500 in the ring stretching region, and a very broad, intense band centered at 990 cm^{-1}. This latter band probably arises from stretching of the C—O group, of an alcoholic type rather than a saturated ether (C—O—C), since the associated ether band at 913 cm^{-1} is not apparent.

These infrared changes are not adequate to identify a specific radiation product nor to demonstrate a definite radiation chemical mechanism. However, the spectra do show that the polymeric product is not that of either of the chemical resinification reactions proposed in the literature.

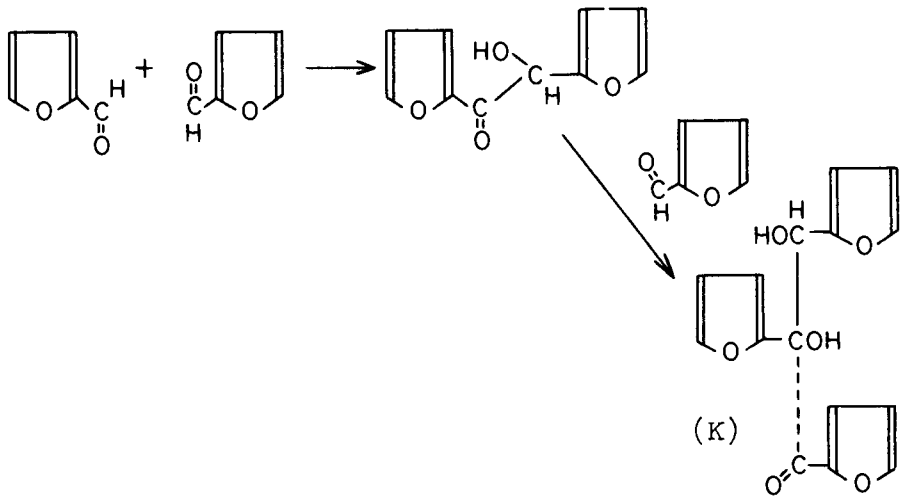
Under conditions of acid hydrolysis, ring cleavage, elimination of formic acid and conversion of carbonyl groups to hydroxy groups have been proposed.[17] The proposed product, (J), would not give the spectra we

(J)



have observed, since there is no furan ring nor other olefin groups.

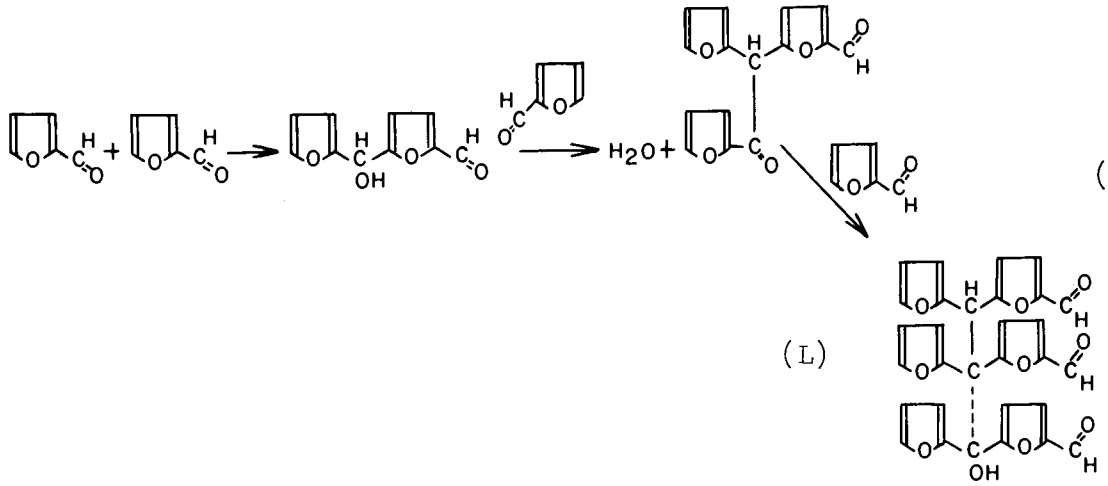
A benzoin type condensation, Reaction 4, giving (K) does not appear



(4)

probable because insufficient CHOH groups are produced to give the 2930 CH stretching band. Furthermore, the substituents on the furan ring are not altered enough to explain the reductions in the 1570 and 1460 bands and the new band at 1500 cm^{-1}.

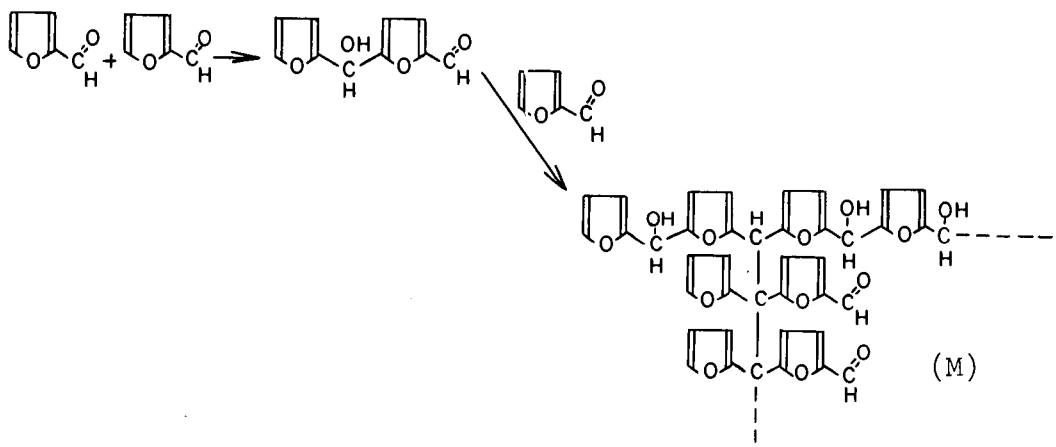
The second resinification reaction proposed in the literature involves addition of the ring H atom in the 5 position to the carbonyl group and the elimination of water with a second aldehyde group[18], Reaction 5, to give (L). This structure gives the requisite changes in substitution on the furan ring to account for the changes in the ring stretching bands at 1570, 1460, and 1500, but the growth in alcoholic



(5)

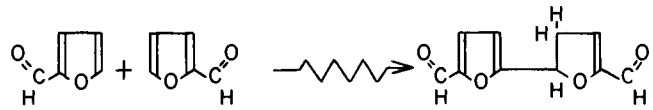
OH and C—O bands at 3450 and 990 cm^{-1} hardly seems explained. In addition, there is no conversion of aldehyde C—H (2820) to alcohol CHOH at 2930 as required by the changes in the C—H stretching region.

A condensation reaction similar to Reaction 5 producing (L), but not involving the elimination of —OH in the dehydration step can be combined with Reaction 5 to produce a crosslinked polymer (M) which would have the molecular structure to give the spectral features observed in the radiation product (Reaction 6).



(6)

To account for the new C=C stretching band at 1620 cm^{-1}, a small amount of addition at the 4 and 5 ring positions can be proposed, Reaction 7.



(7)

This type of addition product could be an integral part of the polymeric product (M) by linking through the carbonyl group.

To augment the I.R. analysis of the polymer, numerous N.M.R. analyses of both furfural and the polymer were run in various solvents. The polymer exhibited a detectable spectrum only upon heating. This spectrum showed an anomalous absorption that had many of the characteristics of water. However, a Fischer titration analysis for water showed the water content of the polymer to be $\approx$ 1%. Therefore, the anomalous peak does not appear to be H_2O. After repeated trials in different solvents it was concluded that the polymer is too insoluble in organic solvents at ambient temperatures to yield a meaningful spectrum. This is characteristic of a highly crosslinked network.

Since oxygen is known to be a radical and electron scavenger, its influence on the radiation-induced polymerization may assist in the interpretation of the mechanism. Therefore, a freshly distilled sample of furfural was irradiated at room temperature with air bubbling through it at a rate of approximately 5 ml/min. A dose of 740 Mrads converted the sample to a dark-colored gel. Within experimental error this was the same gelation dose as required for evacuated samples of both purified and unpurified furfural. A control sample (unirradiated) through which air was bubbled gave no gel. Again, I.R. spectra of the gel and evacuated solid polymer were taken and were identical with those of samples irradiated in the absence of air. Furthermore, the percent conversion (30%) was identical (within experimental error). It thus appears that air has no effect upon the radiation-induced polymerization of furfural. The absence of an oxygen effect on the polymerization suggests that a molecular cationic or anionic species is involved in the rate-determining step. Addition reactions of excited molecules also could proceed without inhibition by oxygen.

A thermogravimetric analysis of the polymer from the air-irradiated polymer showed no plateaus in the weight loss vs temperature curve which indicates there is little or no free furfural or water entrapped in the polymer.

An elemental (C, H, O) analysis was also carried out on the same material. After the analysis was corrected for the water-content analysis

(see above) the results were

$$C\ \% = 60.7$$
$$H\ \% = 4.7$$
$$O\ \% = 32.1\ .$$

This analysis corresponded to a formula of $(C_5H_{4.7}O_2)$. Furfural has an elemental formula of $C_5H_4O_2$. Thus, it appears that there is more hydrogen in the polymer than in the monomer. Confirmatory analyses were not run so this degree of hydrogen enrichment should not be regarded as conclusive. A material balance is difficult to achieve with the probable radiation-induced reactions of furan alone. A possible process is evolution of C=O with absorption of oxygen from the air to maintain the 2:5 oxygen-carbon ratio. This process would be complex and should be regarded as highly speculative until confirmatory evidence is available. In any case, such a general disruption of the furfural molecule must be only a secondary portion of the polymerization reaction since the infrared spectrum can be accounted for without invoking oxidation and elimination of C=O.

Decoloration (Bleaching)

After storage under ordinary conditions, furfural is a dark brown opaque liquid. It was noted that irradiated samples containing furfural were of lighter, transparent color than the unirradiated ones. The extent of the bleaching varied with dose and the age of the unpurified aldehyde. Samples from older stock having more chromophoric impurities were bleached much less than fresher samples for a given dose. Most of the decoloration occurred at doses of 5-10 Mrads and extended irradiation (to 50 Mrads) produced relatively little further decoloration. A colorless vacuum-distilled sample of furfural was given a dose > 100 Mrads, and it was evident that irradiation induced color in the purified sample. Thus it appears that in impure furfural which is partially bleached, a state is approached in which chromophore production and destruction are competitive. As the partial bleaching required a rather large dose and the bleaching was negated upon extended atmospheric exposure, further interest in bleaching experiments was not warranted.

Low-Temperature Irradiation

As certain aldehyde systems are reported to polymerize readily when irradiated at low temperatures,[19,20,21] a sample of furfural was irradiated to 22 Mrads at liquid nitrogen temperature (-196°C). Two other samples, binary mixtures of DMSO and furfural (1:10 and 1:4), were irradiated at this temperature to 30 and 66 Mrads, respectively. None of these low-temperature experiments exhibited any enhanced polymerization yields and it was noted in passing that color bleaching of the furfural was much less than for the same doses at room temperature.

Systems Involving Tetrahydrofurfuryl Alcohol

Samples of tetrahydrofurfuryl alcohol (THFA), in as-received condition, were degassed and sealed in capsules in the same manner as the furfural specimens. These THFA specimens were irradiated at room remperature under the usual conditions to 45 and 95 Mrads. Three decomposition peaks (one relatively large, two small) showed up on a chromatogram employing the silicone rubber column. The major peak corresponded to a small impurity peak in the unirradiated alcohol. As in the case of the furfural, negligible amounts of products having longer retention times than the starting material were observed under these analysis conditions.

Furfural (as-received) was used to prepare a series of solutions of THFA in the aldehyde ranging from 1:1 to 1:100 mole ratio. These were irradiated at room temperature to a dose of ≈ 100 Mrads. As expected from the individual radiolysis, gas chromatography showed that a number of fragmentation products resulted from the mixtures but only small or negligible amounts of self-addition or co-addition products were indicated under the analysis conditions used.

Furan Chemicals with 1,3-Pentadiene (Piperylene)

As conjugated diolefins are chemically reactive,[22] it was decided to investigate their binary mixtures with some furan derivatives in the hope of obtaining high radiolytic yields. A sample of 1:2 mole ratio 1,3-pentadiene-furfuryl alcohol was irradiated to ≈ 700 Mrads. After this rather high dose, the sample was a yellowish, viscous liquid, indicating the presence of appreciable high molecular weight reaction

products. A portion of this sample was then analyzed on a chromatographic column containing polyphenyl ether (11% by weight) on Celite-545. Because products of molecular weight greater than the original were of prime interest, a very short column (14" long) was used to facilitate the passage of products of low volatility.

Retention times for both the initial compounds were very short (<45 seconds) at temperatures as low as 60°C. Despite the short retention times, no significant amounts of addition products such as dimers or trimers were observed for a 1.5-hr chromatogram at a temperature of 175°C. Comparison of peak areas by planimeter measurements indicated that ≃80% of the irradiated sample was retained on the column. The percent of olefin eluting was very small (≈1%) indicating that most of it was incorporated in the non-volatile product.

The injections and analysis were repeated on a column of 5% Apiezon L on Celite-545. The elution pattern on this non-polar column gave essentially the same results as the previous column, no products of molecular weight higher than the original compounds. Although dimeric and trimeric products were not observed with either column, there is the possibility that these products were present in the irradiated sample but underwent reactions on the hot column packing leading to irreversible absorption. On the other hand, since the presence of high molecular weight products is shown by the viscosity of the irradiated sample, it is probable that the initial radiation-induced reaction proceeded directly to the polymeric stage without a terminating step at the dimer or trimer species.

The peak area measurements above indicating that 80% of the original reagents have been converted to non-volatile compounds can be used to calculate radiation yields, if the chromatographic measurements are valid indications of the content of original compounds. This appears to be a reasonable assumption since their chromatographic retention times are so short that it is unlikely that they react in the column. Under this assumption, the G value for consumption of original reagents is 13 molecules per 100 ev.

To conclude the study of mixtures of the furan derivatives with pentadiene, solutions of the diene in tetrahydrofurfuryl alcohol and in furfural, 1:4 mole ratio, were irradiated at room temperature to doses

of about 100 Mrads. Chromatograms of these samples on the Apiezon L column showed only small yields of products having greater retention times than the original reagents. At this moderate dose there were no indications of formation of polymeric products.

SUMMARY AND CONCLUSIONS

The irradiation conditions and the results of the examination of the samples are listed in Table 2. The results for each system are summarized below.

Tetrahydrofuran and Dimethyl Sulfoxide: These reactants did not give high yields of dimeric products ($G < 5$) either as a solution of DMSO in THF or alone. The major products were decomposition products and appeared to be the same whether from the solution or from the individual reagents, $G = 4\text{-}10$. In the solution, DMSO inhibits formation of the major high molecular weight radiation product of THF, in some manner which does not involve combination with the THF radical.

Furfural: The major radiation product of furfural, both pure and containing dissolved DMSO, was a solid polymer, but only in moderate yield ($G = 4$). The yield was not sensitive to purity or the presence of O_2. Irradiation at -196°C did not produce a high yield polymerization as occurs when formaldehyde[20] and acetaldehyde[19] are irradiated below their freezing points. In addition, the infrared spectrum of the polymer from furfural shows that it is not a substituted polyoxymethylene like the lower aldehyde polymers. Instead the reaction produces —OH groups and, by inference, probably C—C interunit linkages.

Tetrahydrofurfuryl Alcohol: Upon irradiation this reactant, both alone and in solution in furfural, showed only decomposition products in low or moderate yields.

1,3-Pentadiene with Furan Chemicals: A solution of 1,3-pentadiene in furfuryl alcohol gave little or no dimeric products but gave polymer in moderately high yield, $G \sim 13$. The nature of the polymer was not determined. The results of irradiating solutions of the diene in tetrahydrofurfuryl alcohol and furfural appeared to be similar.

In conclusion, the radiation yields of products in the desired dimeric molecular weight range were not over 5 molecules per 100 ev for

Table 2. Tabulation of Radiation-Induced Reactions of Furan Chemicals

Reactant[a]	Reaction Conditions			Nature of Major Product	Yield of Major Product (G Value)	Yield of Dimeric Product (G Value)
	Purity or Concentration (mole ratio)	Temp. (°C)	Dose 10^7 rads			
THF	As received	25	1.2	Decomp[b]	4-10	<5
DMSO	As received	25	1.2	CH_3SH	4-10	<5
THF-DMSO	1:1	25	1.2	Decomp + CH_3SH	4-10	<5
THF-DMSO	5:1	25	1.2	Decomp + CH_3SH	4-10	<5
Furfural	As received	25	4.5	?	?	<0.2
Furfural	As received	25	74.	Polymer[c]	4	<0.2
Furfural	Distilled	25	72.	Polymer	~4	<0.2
Furfural	With air	25	74.	Polymer	~4	<0.2
Furfural	As received	-196	2.2	Polymer	<6	<0.2
Furfural + DMSO	10:1	-196	3.0	Polymer	<6	<0.2
Furfural + DMSO	4:1	-196	6.6	Polymer	<6	<0.2
THFA	As received	25	4.5	Decomp	?	<0.2
THFA	As received	25	9.5	Decomp	?	<0.2
THFA-Furfural	1:1	25	10.	?	?	<0.2
THFA-Furfural	1:100	25	10.	?	?	<0.2
Pentadiene-FAlc	1:2	25	70.	Polymer	13	<0.2
Pentadiene-THFA	1:4	25	10.	?	?	<0.2
Pentadiene-Furfural	1:4	25	10.	?	?	<0.2

[a]THF-tetrahydrofuran, DMSO-dimethyl sulfoxide, THFA-tetrahydrofurfuryl alcohol, FAlc-furfuryl alcohol.

[b]Products having chromatographic retention times shorter than the original reactants are considered "decomposition" products.

[c]Products of such high molecular weight and low volatility that they will not pass through the chromatograph are termed "polymer." Their yields are calculated as the number of molecules of original reactants incorporated in the polymer.

tetrahydrofuran and its solutions and were less than 0.2 for the other furan chemicals investigated. Furfural gave polymer in moderate yields (G = 4) and solutions of 1,3-pentadiene in furan chemicals gave polymeric products in considerably higher yields (G = 13). On the other hand, both furfural and 1,3-pentadiene are capable of polymerization under chemical initiation or catalysis and no advantages were observed for the radiation-induced reactions. Because of the low yields of dimeric and trimeric products and because of the lack of any superior features in the polymeric products, no processes of commercial potential are apparent in this investigation.

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